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STANDARD OPERATING PROCEDURE

# SULFIDES, ACIDS VOLATILE

GEN-AVS
Revision 6

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Approved By:

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# SULFIDES, ACIDS VOLATILE

## 1. SCOPE AND APPLICATION

1.1. This procedure describes the determination of acid volatile sulfide (AVS) in soil, sediment, and other solids. As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in sediments. The procedure can be used to isolate those metals, referred to as Simultaneously Extracted Metals (SEM), solubilized during the acidification step. Analysis for these metals can then be done using the applicable metals determinative procedure.

1.2. Research has established that the relative amounts of SEM and AVS are important in the prediction of potential metal bioavailability; if the molar ratio of SEM for bivalent metals to AVS exceeds one, the toxic heavy metals in that sample are potentially bioavailable. This method uses the same conditions for release of both sulfide and metal from the sediment and thus provides a useful means of assessing the amount of metal associated with sulfide.

1.3. This procedure also includes steps for determination of Chromium Reducible Sulfur.

1.4. This method is capable of determining sulfides in the range of 0.5 mg/Kg to 30,000 mg/Kg dry weight. The Method Reporting Limit (MRL) 0.5 mg/Kg. Method detection limits are 0.05 mg/Kg in the sample.

## 2. METHOD SUMMARY

2.1. The AVS in the sample is first converted to hydrogen sulfide ($H_2S$) by acidification with hydrochloric acid at room temperature. The $H_2S$ is then purged from the sample and trapped in aqueous solution. The amount of sulfide that has been trapped is then determined. If SEM is to be determined, a portion of the aqueous solution is used to perform selected metals analyses.

2.2. The $H_2S$ released by acidifying the sample is quantified using a colorimetric procedure. In the colorimetric method, the $H_2S$ is trapped in sodium hydroxide. The sulfide reacts with N-N dimethyl-p-phenylenediamine to form methylene blue that is measured. This procedure is capable of determining AVS concentrations as low as 0.5 mg/Kg dry weight of sediment. By appropriate sample dilution, the maximum concentration of AVS which can be determined is at least 30,000 mg/Kg dry sediment.

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## 3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, meeting the criteria in Section 3.3 and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.2. **Sample**

3.2.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid point of the calibration range or at levels specified by a project analysis plan.

3.5. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and

analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8. Acid Volatile Sulfide (AVS) - AVS is defined as sulfides that form hydrogen sulfide under the conditions of this test. This includes amorphous, moderately crystalline monosulfides, and other sulfides.

3.9. Method Detection Limit (MDL) - The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined as described in the SOP for The Determination of Method Detection Limits.

3.10. Stock Standard Solution - A concentrated solution of the analyte prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.

3.11. Calibration Standards - Solutions prepared from the stock standard solution that is used to calibrate the method response with respect to analyte concentration.

## 4. INTERFERENCES

4.1. Contact with oxygen must be avoided in all stages from sampling to analysis. Consequently, the samples and standards should be protected from air from the time of sampling through the analytical procedure.

4.2. Carbonation is an interference that can occur when acid is added to the sample. The carbonation can push the sulfide into the B tower or outside it. To prevent this, acid should be added to the sample slowly and/or the sample weight reduced.

## 5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

5.4. Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while

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pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

5.5. Hydrogen sulfide is a highly poisonous, gaseous compound having a characteristic odor of rotten eggs. It is detectable in air by humans at a concentration of approximately 0.002 ppm. Handling of acid samples should be performed in a hood or well ventilated area. If a high concentration of hydrogen sulfide is detected in the air by the laboratory staff, sample handling procedures must be corrected. Exposure to $H_2S$ in air must not exceed guidelines or regulations. The OSHA Permissible Exposure Limit (PEL) is 50ppm.

5.6. If samples originate from a highly contaminated area, appropriate sample handling procedures to minimize worker exposure must be followed.

## 6. SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1. Sulfide ion is unstable in the presence of oxygen. Protect sediment samples from exposure to oxygen during sample collection and storage.

6.2. During storage, sulfide can be formed or lost due to biological activity, and sulfide can be lost by volatilization or oxidation. Metal speciation can change as a result of changes in sulfide concentration and as a result of other changes in the sample.

6.3. Samples should be collected in wide mouth jars with a minimum of air space above the sediment. If possible, the headspace should be filled with oxygen free nitrogen or argon. The jar lids must have Teflon or polyethylene liners.

6.4. Samples should be cooled to 4 ± 2 °C as soon as possible after collection. Samples maintained at 4 ± 2 °C have been found to have no significant loss of AVS for storage periods up to 2 weeks. Holding time for samples should not exceed 14 days.

## 7. APPARATUS AND EQUIPMENT

7.1. Glassware

7.1.1. AVS evolution and $H_2S$ trapping - The Midi is typically used.

7.1.1.1. Midi setup: For each analytical train, use one boiling tube attached to an inlet adapter that is topped with a 50 ml dropping funnel. This apparatus is connected to a fritted bubbler (called the “A” tower) which is then connected by tubing to the “B” tower. The boiling tube contains the sediment and acid is introduced to it by the 50 ml dropping funnel. Because sulfide may react with tubing and other surfaces, minimum lengths of tubing should be used as sleeves to connect the glass tubing.

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7.1.1.2. Macro setup: For each analytical train, one 500 ml round bottom flask with a septum 250 ml scrubber towers with impingers with non-fritted outlets. The round bottom flask contains the sediment and acid is introduced to it by a syringe inserted through the septum. The flasks are connected by tubing. Because sulfide may react with tubing and other surfaces, minimum lengths of tubing should be used as sleeves to connect the glass tubing. The analyst should pay particular attention to the recovery of sulfide from standards in evaluating the apparatus.

7.1.1.3. The analyst should pay particular attention to the recovery of sulfide from standards in evaluating the apparatus used.

7.1.1.4. In all cases, the inlets are below the liquid level and the outlets are above the liquid levels. The apparatus is assembled as shown in Figure 1, and more than one analytical train can be connected to a single cylinder of nitrogen or argon if flow controllers are installed in the line.

7.2. Assorted calibrated pipettes and volumetric flasks.

7.3. Evergreen disposable tubes, 50 mL. Check tubes for accuracy on a per batch basis by filling a tube to the 50 mL mark and measuring the water's mass. The measured mass must be accurate to ± 3%, if not obtain a new lot of tubes and retest. Refer to the SOP for *Checking Volumetric Labware (ADM-VOLWARE)*, for detailed instructions on performing the accuracy test.

7.4. Analytical balance - capable of weighing to 0.0001 g.

7.5. Magnetic stirrer, thermally insulated and Teflon-coated stirring bar.

7.6. Spectrophotometer - Capable of measuring absorbance at 670 nm.

7.7. Spectrophotometer cells, 1mm.

## 8. STANDARDS, REAGENTS AND CONSUMABLE MATERIALS

8.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking (ADM-RTL)* for the complete procedure and documentation requirements.

8.2. All water and reagents used in this method must be free of dissolved oxygen and sulfide. Prepare reagents fresh for each batch and use deaerated, deionized water by removing dissolved oxygen from the deionized water by vigorously bubbling with oxygen-free

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nitrogen or argon for approximately one hour. Deaerate reagents immediately before use by deaerating with oxygen-free nitrogen or argon.

8.3. Sulfide stock standard solution, approximately 0.05M or 50 µmoles/ml.

8.3.1. Weigh about 5.25 gram of $Na_2S{\cdot}9H_2O$ and dissolve it in 250 ml of 0.5N NaOH. Store in a brown bottle. To prevent air oxidation, the sulfide solution should be maintained under oxygen-free nitrogen or argon. This solution must be standardized daily against thiosulfate to quantitatively determine sulfide concentration. Provided that the solution is standardized daily, at the time of use, the sulfide stock solution may be used for up to six months.

8.3.2. Standardize against thiosulfate solution.

8.3.2.1. Pipette 11.0 ml of 0.025N standard iodine solution into each of two 125-ml Erlenmeyer flask or beakers.

8.3.2.2. Pipette 1.00 ml of sulfide stock standard solution into one flask. Pipette 2.00 ml of deionized water, as a laboratory reagent blank, into the other flask.

8.3.2.3. Add 5.00mL of 6M HCl into each flask, swirl slightly.

8.3.2.4. Titrate each with 0.025N thiosulfate until the yellow iodine color fades to a pale straw. Just before all the iodine has been titrated, add starch indicator dropwise to form a pale blue color. Continue the titration with the thiosulfate. The end point is reached when the blue color first disappears.

8.3.2.5. Calculate the sulfide concentration as follows:

$$Sulfide\,(mg/L) = \frac{\left[\left(mL\ of\ I_2\ x\ N\ of\ I_2\right) - \left(mL\ of\ titrant\ x\ N\ of\ titrant\right)\right] x\,16030}{Volume\ of\ std}$$

8.4. Iodine Solution (approximately 0.025N)

8.4.1. Dissolve 25 g potassium iodine, KI, in 700 ml of reagent water in a 1 liter volumetric flask. Add 3.2 g iodine, $I_2$. and allow to dissolve. Add 2 ml of 6N HCl and dilute to 1.0L with reagent water. Standardize against sodium thiosulfate as follows.

8.4.2. Titrate until amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

8.4.3. Run in duplicate

8.4.4. Calculate the normality as follows:

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$$\frac{mls\ S_2O_3\ x\ Normality\ of\ S_2O_3 (0.025N)}{mls\ Iodine\ titrated\ (5\ mls)}$$

8.5. Standard sodium thiosulfate solution (0.025N): Dissolve 6.205 ± 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 ml reagent water. Add 18 ml of 0.5N NaOH, and dilute to 1 liter.

8.6. Starch indicator - Dissolve 1.0 gram soluble starch in 100 ml boiling deionized water.

8.7. Sulfide working standards - Prepare sulfide working standards using the sulfide stock standard solution in Section 8.3.1. The concentrations of the following standards will depend on the exact concentration of the sulfide stock standard determined in Section 8.3.2.5.

Prepare the sulfide working standard by diluting 1.00mL of sulfide stock standard to 100mL 0.5N NaOH. This solution contains 28.0 mg sulfide/L, if the concentration of the sulfide stock standard is exactly 2800 mg/L. This working solution must be prepared daily from standardized stock solution.

8.8. AVS Evolution reagents

8.8.1. Hydrochloric acid 6M - Dilute 500 ml of concentrated hydrochloric acid to 1.0 L de-aerated reagent water.

8.8.2. Nitrogen gas, oxygen free, with regulator and flow controller.

8.8.3. Plastic hypodermic syringe, 30 ml, and needle.

8.9. Colorimetric reagents

8.9.1. Sodium Hydroxide solution, 0.5N - Dissolve 20 g sodium hydroxide per 1000 ml reagent water. Generally make 4.0 L at one time. (80 g NaOH to 4.0 L)

8.9.2. Mixed diamine reagent, MDR

8.9.2.1. Component A - Add 1320 ml concentrated sulfuric acid to 680 ml of reagent water after solution cools, dissolve 4.50 g N-N-dimethyl-p-phenylenediamine oxalate in it.

8.9.2.2. Component B - Dissolve 10.87 g ferric chloride hexahydrate ($FeCl_3 \cdot 6\ H_2O$) in 200 ml concentrated hydrochloric acid and dilute to 400 ml with reagent water.

8.9.2.3. Mixed diamine reagent, MDR – Slowly mix 2 L component A and 400 mL component B the components A and B (prepared above) and allow to cool.

8.10. Sulfuric acid solution, 1.0M – Dilute 56 mL concentrated $H_2SO_4$ to 1L reagent water.

8.11. Reagent required for Chromium Reducible Sulfur (Fossing & Jorgensen)

8.11.1. Ethanol, purchased commercially at ≥95% purity.

8.11.2. Concentrated hydrochloric acid (HCl)

8.11.3. Hydrochloric acid, 1N, purchased.

8.11.4. $Cr^{+2}$ solution: Prepare from $Cr^{+3}$ by dissolving 133.2g of Chromium (III) chloride hexahydrate in 500mL of 0.5N HCl. The $Cr^{+3}$ solution is poured over 1N HCl washed mossy zinc in a nitrogen glove box and let sit until the solution turns a deep blue color. At this time the solution can be filtered into glass jars and nitrogen capped until ready to use. The solution will remain blue for a number of days. Remake standard if color fades or after one month, which ever comes first.

## 9. RESPONSIBILITIES

9.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

9.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP for Documentation of Technical Personnel Training is also the responsibility of the department supervisor/manager.

## 10. PREVENTIVE MAINTENANCE

10.1. No specific maintenance steps are needed other than normal cleaning and inspection of apparatus.

10.2. Wipe down the Midi unit after use to remove any residual acid.

## 11. PROCEDURE

Note: Refer to Appendix A if Chromium Reducible Sulfur is to be determined.

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11.1. Macro distillation procedure

11.1.1. Place two neck flasks on stir plates and clamp into place.

11.1.2. Add one stir bar and 100 ml of reagent water to each flask. The amount of water added and the water present in the wet sediment should not exceed 120 mls.

11.1.3. Add 80 mls of 0.5N NaOH to each of the two towers for each flask. Label the first tower A, the second tower B.

11.1.4. Place septum stopper and impinger in two-neck flask. Place tower scrubbers in towers and connect the glassware with the tubing.

11.1.5. Purge the system with $N_2$ gas for approximately 10 minutes.

11.1.6. Weigh 10 g of wet sediment onto a 2x2 inch piece of parafilm. Remove the septum stopper and place the parafilm with sample into the flask. Do not rinse sample into flask. Purge the system for another 10 minutes.

Stop the flow of gas. Using the 30 ml hypodermic syringe, add 20 ml of 6M HCl to the flask via septum. Bubble nitrogen through the system for one hour while constantly stirring. For the LCS and spike, add the appropriate amount of sulfide standard before adding the acid.

11.1.7. Calibration and Standardization

11.1.7.1. Prepare a sulfide curve as follows:

11.1.7.1.1. Add 80 mls of 0.5N NaOH to each of 7 - 100 ml volumetric flask.

11.1.7.1.2. Using working standard A, add 0.0 ml, 1.0 ml, 2.0 ml, 1.0 ml, 3.0 ml, 4.0 ml and 5.0 ml to flask. Bring to 100 mL final volume using 0.5 N NaOH.

11.1.7.1.3. Calculate concentration of standards as follows:

$$\frac{\textit{(mls STD added) x (Conc. Of STD)}}{\textit{Final volume (100ml)}} = ____\textit{mg/L}$$

Example: $\frac{4.0\text{ml} \times 28.0\text{ mg/L}}{100\text{ml}} = 1.12\text{ mg/L}$

11.1.7.1.4. Use the 0 ml STD for the CCB and the 4 ml STD for the CCV.

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11.1.8. After one hour has elapsed, remove the scrubber from tower B and transfer to a 250 ml plastic container. Repeat for tower A. Leave $N_2$ gas flowing through scrubbers so that the NaOH does not go back up into the scrubber.

11.1.9. Disconnect tubing from flow meter at the flask impinger and then turn off the $N_2$ at the flow meter. This prevents liquid from backing up into the flow meter and destroying it.

11.1.10. Proceed to section 11.3.

11.2. Midi distillation procedure

11.2.1. Soak the scrubbers in 10% nitric acid and then rinse scrubbers with 10% nitric acid followed by a rinse with deionized water.

11.2.2. Place analytical train, consisting of the boiling tube, inlet adapter and 50 ml dropping funnel, into the midi apparatus.

11.2.3. Add 40mL of 0.5N NaOH to each bubbler vessel and clamp scrubber to bubbler vessel. Connect scrubber, with bubbler vessel attached, to the analytical train.

11.2.4. Purge the system for approximately 10 minutes.

11.2.5. Add 10.0g of sample (or less depending on expected sulfide concentration) to the boiling tube. Rinse sample to the bottom of the boiling tube with 40mL of reagent water. Make sure no sample remains above the reagent water level. Clamp the impinger to the boiling tube.

11.2.6. Calibration and Standardization

11.2.6.1.Prepare a sulfide curve as follows:

11.2.6.1.1.Add 35 mls of 0.5N NaOH to each of 7- 50 ml centrifuge tubes.

11.2.6.1.2.Using working standard A, add 0 ml, 0.05 ml, 0.5 ml, 1.0 ml, 1.5 ml, 2.0 ml and 2.5 ml to each tube. Bring to 50 mL final volume using 0.5 N NaOH.

11.2.6.1.3.Calculate concentration of standards as follows:

$$\frac{\text{(mls STD added) x (Conc. Of STD)}}{\text{Final volume (40ml)}} = ____\text{mg/L}$$

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Example: $\frac{2.5\text{ml} \times 28.0\text{ mg/L}}{40\text{ml}} = 1.75\text{ mg/L}$

11.2.6.1.4. Use the 0 ml STD for the CCB and the 1.5 ml STD Check for the CCV.

11.2.7. Purge system for 10 minutes.

11.2.8. Connect scrubber tube with a disposable pipet to scrubber extension. Place the pipet into 50mL centrifuge tube filled with 40mL of 0.5N NaOH. (These are the "B" towers.)

11.2.9. Purge for 10 minutes.

11.2.10. Add the LCS and the Spike(s).

11.2.10.1. For aqueous blank spikes, add 2mL of the sulfide working standard to 50mL of purged reagent water.

11.2.10.2. For soils and solids, weigh 10g of analyte-free glass beads and add 50mL of reagent water. Purge for 10 minutes, then add 2mL of the sulfide working standard.

11.2.10.3. For matrix spikes, spike the sample with 1mL of the sulfide stock standard.

11.2.11. Add 10.0 mL of 6N HCl to each boiling tube through the 50 ml dropping funnel.

11.2.12. Let system react for 1 hour.

11.2.13. Place scrubber solution from bubbler vessels into separate containers. Before screwing on the cap, cover each solution with nitrogen. The same procedure is used for B towers except that the scrubber solution is left in the original centrifuge tube.

11.2.14. After complete, take down the apparatus and rinse all parts with water. Use a damp paper towel to wipe down midi still and surrounding area.

**Note:** If Simultaneously Extracted Metals are to be determined, decant bubbler tube to 100 ml graduated cylinder, dilute to volume with water and pour into an acid cleaned plastic storage container for metals analysis.

11.3. Color development and analysis

11.3.1. If the sample is known or suspected to fall within the range of the curve, transfer the entire volume of tower A to a 50 ml centrifuge tube. Transfer 20 ml of the solution

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to a 30 ml centrifuge tube, add 2.5 ml of MDR and dilute to 25 ml with reagent water. For the six standards for the curve, add 5 ml MDR to 40 ml standard and dilute to 50 ml with reagent water in 50 ml centrifuge tubes.

If the samples are known or are suspected to be high in concentration, dilutions may be performed in 0.5N NaOH. Add 5 ml MDR to 40 ml diluted sample and dilute to 50 ml with reagent water.

11.3.2. If blue color change develops in the sample, the scrubber solution of tower B for that sample must also be analyzed. If no color change occurs for tower A, then tower B does not have to be analyzed.

11.3.3. For tower B add 5 ml MDR and dilute to 50 ml with reagent water.

11.3.4. After adding the MDR, allow a full thirty minutes for color development, but read the samples before 2 hours have elapsed.

11.3.5. Allow a thirty minute warm-up of the spectrophotometer. Zero the instrument with D.I. water at 670.0 nm.

11.3.6. Calibrate the instrument with the prepared curve starting with the low standard. A calibration with a correlation coefficient (r) of $\geq 0.995$ must be obtained. Corrective action for a correlation coefficient $< 0.995$ is to discard existing curve, obtain new volumetrics and make a new curve. Verify concentration of stock sulfide standard.

11.3.7. Analyze samples in the following order:

| Analysis | Sample |
|---|---|
| 1 | CCV-1 |
| 2 | CCB-1 |
| 3 | LCS-1 |
| 4 | MB-1 |
| 5 | Sample-1 |
| 6 | Sample-1D |
| 7 | Sample-1S |
| 8 | Sample-1SD |
| 9-11 | Sample 2 - 4 |
| 12 | CCV-2 |
| 13 | CCB-2 |
| 14 -23 | Sample 5 - 14 |
| 24 | CCV-3 |
| 25 | CCB-3 |

11.3.8. Analyze a continuing calibration verification standard (CCV) and continuing calibration blank (CCB) every 10 sample or QC analyses. The CCV is the fifth point

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on the curve. The CCV must be ± 10% of the expected value. If the CCV fails, then the curve is not correct. The correlation coefficient may be ≥ 0.995, but if the slope is to high or too low, then the CCV will not pass. Notify supervisor, re-make the curve and re-calibrate.

11.3.9. The CCB must be < 0.05 ppm - The CCB is the first point of the curve.

11.3.10. Calculate AVS concentration as follows:

$$\frac{(Conc.\ from\ curve)(DF)\ x\ Final\ volume}{Initial\ wt\ \ x\ \%solids.} = mg/Kg\ AVS$$

11.3.11. Final volume when doing this procedure is 40 mL using the Midi apparatus and 100 mL using the Macro distillation procedure.

## 12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this four analyte free glass beads are spiked with the LCS spike solution, then prepared and analyzed. For each analyte the mean recovery of the true value should be 60-130%, and the RSD should be ≤ 20%.

12.2. Method Detection Limits and Method Reporting Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2. Calculate the average concentration found in *mg/Kg AVS*, and the standard deviation of the concentrations (s) in *mg/Kg AVS.* Calculate the MDL for each analyte. Refer to the CAS *SOP Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification (ADM-MDL).* The MDL study must be verified annually.

12.2.3. Limits of Quantification (LOQ)

12.2.3.1. The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the

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calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 50-150% of the true values to verify the data reporting limit. Refer to the CAS SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification (ADM-MDL)*

12.2.4. The Method Reporting Limits (MRLs) used at CAS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which CAS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3. Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). General QC Samples are:

12.3.1. A method blank (MB) for every 20 samples analyzed.

12.3.2. One LCS for every 20 samples analyzed. Due to the time requirements for set-up and distillation, it is best to distill 2 LCS's for every 20 samples. Sulfides are very unstable and easily degraded and therefore it is not uncommon to have low sample recoveries.

12.3.3. Analyze one matrix spike and one matrix spike duplicate per 20 samples minimum.

12.3.4. Analyze one sample duplicate for every 20 samples minimum.

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12.4. Acceptance Criteria

12.4.1. The method blank (MB) must be < MRL. If MB > MRL, reanalyze MB and all samples associated with the MB. If problems persist, attempt to determine source of contamination and perform reanalyses as necessary.

12.4.2. The MRL is calculated as follows:

$$\frac{0.05\ mg/L\ x\ Final\ volume(L)}{Initial\ wt.(kg)\ x\ \%solids}$$

12.4.3. The LCS must be 60-130% of the expected value. If the LCS recovery is outside of the criteria, sulfides were lost at some point during distillation, or sample was spiked at the improper level. Re-analyze LCS and all samples associated with that LCS. (Note - LCS's generally only fail high if the sample was spiked too high).

12.4.4. Matrix Spike recovery criteria is 30-160% recovery. If the recovery is outside the criteria, re-analyze spike. If two spikes were analyzed initially, then matrix interferences caused low spike recoveries. No need to reanalyze at that point.

12.4.5. The relative percent difference (RPD) for duplicates should be ≤ 20% RPD. If the RPD is > 20%, verify homogeneity of sample. Reanalyze the duplicate. Calculate RPD as follows:

$$RPD = \frac{High\ value\ -\ Low\ value}{Average}\ x\ 100$$

## 13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Calculate samples results as described in section 11.6.12. Results for QC analyses are calculated and recorded as specified in section 12. Average, RPD, spike level and spike recovery are entered on benchsheet for corresponding samples. All data will be initialed, dated and attached to required data quality worksheet.

13.2. The appropriate benchsheets, located in Attachment A, should be in use at all times during AVS analysis.

13.3. The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the CAS network directory R:\WET\WIP. These forms are made from templates located in R:\WET\FORMS.

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13.4. Data Review and Assessment

13.4.1. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process (ADM-DREV)* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative.

13.5. Reporting

13.5.1. Soils, sediments, and other solid matrices are reported as µmol/g, either dry weight or as received, according to the project requirements.

AVS, µmol/g = (mg/Kg AVS in sample)/ [(32 g/mol S) (dry weight ratio) (sample weight g)]

13.5.2. The MRL is calculated as follows:

$$\frac{0.05\ mg/L\ x\ Final\ volume(L)}{Initial\ wt.(kg)\ x\ \%solids}$$

13.5.3. The MRL will vary depending on % solids content. For samples reported as received, the MRL = 0.05 mg/Kg.

13.5.4. For samples that did not require a dilution, 3 significant figures will be reported. For samples that required a dilution, report only 2 significant figures.

## 14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Corrective Action (ADM-CA)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance log books, run logs, for example.

14.2.2. Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when:

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- Corrective action is not taken or not possible
- Corrective action fails to correct an out-of-control problem on a laboratory QC or calibration analysis.
- Reanalysis corrects the nonconformity but is not a procedurally compliant analysis.

## 15. METHOD PERFORMANCE

15.1. Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as specified in Section 12.1. The method detection limit(s) and method reporting limit(s) were established for this method as specified in Section 12.2.

## 16. POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

## 17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 5-9 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details.

17.3. This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 5-9 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details

## 18. TRAINING OUTLINE

18.1. Training outline – Training Plan

18.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these

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reviews, observe the procedure as performed by an experienced analyst at least three times.

18.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of two months. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

18.1.3. Perform an Initial Demonstration of Capability (IDOC) as described above. Summaries of the IDOC are reviewed and signed by the departments Technical Services Manager. Copies of the IDOC and Training Plan are forwarded to QA for record keeping. For applicable tests, IPR studies are performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

18.1.4. Training is documented following the SOP *for Documentation of Training*.

18.1.4.1. When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

## 19. METHOD MODIFICATIONS

19.1. No method modification noted for Revision 6 of this SOP.

## 20. REFERENCES

20.1. *Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment,* June, 1997 ;
*EPA Method 1629.*

20.2. *Measurement of Bacterial Sulfate Reduction in Sediments: Evaluation of a Single-step Chromium Reduction Method*, Henrik Fossing and Bo Barker Jorgensen, 1989, *Biochemistry*.

## 21. CHANGES SINCE THE LAST REVISION

21.1. Sec 1.4 - Removed the third sentence that was in previous revision
21.2. Sec 3.1 – 3.7 is new
21.3. Sec 7.1.1.1 – corrected and updated how to set up Midi still
21.4. Sec 7.3 is new
21.5. Sec 8.1 is new
21.6. Sec 8.3.2.1 changed 10 mL to 11 mL and added *or beakers*

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21.7. Sec 8.4.4 – corrected equation
21.8. Sec 8.9.2.2 – changed 10.8 to 10.87
21.9. Sec 11.2.1 replaced 6 N HCL with 10% HNO3
21.10. Sec 11.2.2 – replaced the word system with apparatus
21.11. Sec 11.2.6 is new
21.12. Sec 11.2.10.2 – replace sand with glass beads
21.13. Sec 11.2.14 – NOTE updated
21.14. Sec 11.3.3-removed transfer to 30 mL centrifuge tube, changed 2.5 mL to 5.0 and 25 to 50 mL
21.15. Sec 11.3.11 – re-wrote for clarity
21.16. Sec 12.1 – 12.2 is new
21.17. Sec 14 - updated
21.18. Sec 19 and 21 are new

# APPENDIX A

## Procedure for Chromium Reducible Sulfur

1. After removing A-tower scrubbers and B-towers from the AVS distillation, replace them with new A and B towers described in Sections 11.2.3 and 11.2.8.

2. Using a syringe and needle, add 5mL of ethanol to each sample tube through the septum.

3. Purge system for 15 minutes with nitrogen gas.

4. Add 16mL of $Cr^{+2}$ solution to each sample tube through the septum using syringes and needles prepared in the nitrogen glove box.

**Note: The aliquots (in the syringes) of the $Cr^{+2}$ solution must be prepared in the nitrogen glove box to prevent the solution from reducing back to $Cr^{+3}$.**

5. Add 8mL of concentrated HCl using syringes and needles.

6. Distill at room temperature for 15 minutes, then increase the temperature of midi to 90°C. Distill for an additional 45 minutes.

7. The concentration of the A and B towers are determined as for AVS using the procedure in Section 11.3.

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# ATTACHMENT A

## Benchsheet