Method no.:	ID-170SG
Matrix:	Air
OSHA Standard:	0.05 mg/m^3 Uranium, soluble compounds
Collection Procedure:	A known volume of air is drawn through a cassette containing an FWS-B (5 μm) filter and a back-up pad.
Recommended Air Volume:	240 liters
Recommended Sampling Rate:	2.0 liters per minute
Analytical Procedure:	An FWS-B filter is extracted with electrolyte solution. An aliquot of the sample is then analyzed for uranium by the technique of Differential Pulse Cathodic Stripping Polarography (DPCSP), or Differential Pulse Stripping (DPS).
Qualitative Detection Limit:	Estimated to be 0.2 μg for a 10 mL sample.
Precision and Accuracy:	(CV) 0.036 (Analytical)
Method Classification:	Partially Validated
Date:	June 1986

1. Introduction

    1.1. Scope

    This method describes the collection and analysis of airborne particulates containing soluble uranium. The technique used for this analysis is Differential Pulse Cathodic Stripping Polarography (DPCSP). This technique involves the reduction of hexavalent uranium (U^{6+}) on the surface of a static mercury electrode (SME) drop (7.1). The electrolyte solution used in the analysis contains 0.05 M tartaric acid and 0.05 M triethanolamine; it is weakly acidic, with a pH = 3.5. The electrolyte solution is used to extract soluble uranium from the sample filters, because it has been found experimentally to give better recoveries as compared to extraction using deionized water (DIW) (7.2). For this reason soluble uranium is defined in the context of this analytical procedure as that uranium which will dissolve in an aqueous solution containing 0.05 M tartaric acid and 0.05 M triethanolamine. Refer to BUD (7.2) for more details.

    1.2. History

    Uranium samples sent to the OSHA Laboratory have been analyzed by the method of neutron activation (7.3). Using that technique, samples prepared at OSHA must be sent to a local University reactor to be bombarded by neutrons. The uranium can then be quantitated by counting the number of disintegrations occurring at energy levels specific for uranium. This method gives good quantitative results, but it is relatively time-consuming and expensive. Also, samples must be given up for a time to non-OSHA personnel: For these reasons, a polarographic procedure was developed at the OSHA Laboratory.

    1.3. Toxic Effects (7.4, 7.5)

    1.3.1. Toxicity is closely related to solubility, i.e., the more soluble the uranium compound is, the more toxic it becomes.

    1.3.2. Soluble uranium compounds are toxic either when breathed or ingested. The kidney is the organ most directly affected by uranium, which causes tubular degeneration and renal failure.

    1.3.3. The administration of calcium disodium edetate is useful for removing uranium from the body.

    1.3.4. Of the most important uranium compounds used industrially, UF_6 and $UO_2(NO_3)_2 \cdot 6H_2O$ are the most toxic, whereas UO_3 is only moderately toxic, and UO_2, U_3O_8, and UF_4 are considered low in toxicity.

    1.4. Physical Properties (7.4, 7.6, 7.7)

    1.4.1. Uranium, atomic number 92, has an atomic weight of 238. It has a density of 19.05 and a melting point of 1132 °C. It is a silvery, lustrous, malleable, and ductile metal. It occurs in the earth's crust at a concentration of about 2 ppm.

    1.4.2. In the dry state uranium forms compounds having valences of 3+, 4+, 5+, or 6+. In aqueous media only U^{4+} and U^{6+} are stable. Some compounds, such as UCl_4, decompose in aqueous media to the U^{6+} state (see Table 5). In acid solution and in the body, the oxygen-containing cation UO_2^{+2}, where uranium has a valence of 6+, is the predominant form. In general, hexavalent uranium compounds are the most soluble.

2. Range and Detection Limit

   2.1. The working range is from 0.05 ppm to 2.0 ppm uranium.

   2.2. The qualitative detection limit for a 10 mL sample is estimated to be 0.2 µg, based on the lowest quantity of uranium which produces a discernable peak. Refer to Figure 1 in the BUD (7.2) for better illustrative detail.

3. Precision and Accuracy

   3.1. Quantities of soluble uranium were spiked onto FWS-B filters at levels corresponding to 0.5, 1.0, and 2.0 times the OSHA-PEL, based upon a 240 L air sample. At each of the three PEL levels, 6 filters were used, giving a total of 18 filters for a complete set. Two complete sets of filters were analyzed for uranium recovery. Refer to Back-up Data (BUD) for complete results (7.2).

   3.2. The pooled coefficient of variation (CV) for the two sets (n=36), a measure of total analytical precision, was calculated to be 0.036. This value corresponds to a standard deviation of 0.0018 mg/m^3 at the OSHA-PEL standard level.

   3.3. The average recovery for the two sets at the three OSHA-PEL levels (n=36) was 98.4%.

4. Advantages and Disadvantages

   4.1. Advantages

      4.1.1. This procedure is relatively quick, simple, and exhibits good reproducibility over the working range.

      4.1.2. The method of DPCSP saves on mercury by performing a complete analysis with one mercury drop.

      4.1.3. The chain of evidence stays within OSHA, i.e., samples are not sent out of the Laboratory for analysis.

   4.2. Disadvantages

      4.2.1. Small changes in pH (> 0.2 pH) will cause a reduction in signal intensity. This change is minimized by the buffering capacity of the electrolyte solution. However, it is necessary for the analyst to check the pH of each sample with pH paper. If the pH of the sample differs by more than 0.2 pH units from the electrolyte solution, small amounts of acid or base should be added to the sample until its pH is close to that of the electrolyte.

      4.2.2. It has been determined experimentally that the presence of certain ions (Cr^{6+}, Mo^{6+}, Ti^{4+}, and F^-) at concentrations one to four times that of the uranium will also result in a reduction in signal intensity (7.2, 7.8). The three metal cations all have half-wave potentials more negative than that of hexavalent uranium. High concentrations of these interfering cations will produce separate peaks from that of uranium. At concentrations near to that of uranium, however, varying degrees of shoulder-broadening can be seen on the uranium peak.

5. Sampling Procedure

   5.1. Apparatus

      5.1.1. Personal Sampling Pump: A calibrated pump whose flow rate an be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative sampler (filter, sorbent tube, etc.) in line to minimize errors associated with uncertainties in the volume sampled.

5.1.2. Filter holder: A 3-piece polystyrene, 37 mm diameter cassette.5.1.3 Polyvinyl chloride (PVC) membrane filters: 5.0 micron pore size, 37 mm diameter. FWS-B or equivalent.

5.2. Procedure

5.2.1. Sample at a known flow rate of about 2 L/min. A minimum sample size of 100 L is recommended.

5.2.2. Include a blank FWS-B filter with each sample set.

5.2.3. After sampling, plug the cassette ports and seal the cassettes with official seals (OSHA Form 21). Send to the laboratory for analysis.

6. Analytical Procedure

6.1. Apparatus

6.1.1. Polarographic analyzer or controller: Princeton Applied Research (PAR), Model 384-B, or equivalent.

6.1.2. Static mercury drop electrode: PAR Model 303A

6.1.3. Polarographic cells (20-mL). Soak used cells in 6 M HNO_3 for one hour and rinse thoroughly with DIW. Air dry on clean absorbent paper.

6.1.4. Digital plotter: Model DMP-40, Houston Instrument, or equivalent.

6.1.5. Adjustable micropipettes: Gilson P-200 & P-5000, or equivalent.

6.2. Reagents - All chemicals should be ACS reagent grade or equivalent.

6.2.1. Uranium stock solution, 1000 ppm: Purchased from Spex, prepared from HiPure material, in a 2% HNO_3 matrix. This solution is good for one year.

6.2.2. Supporting electrolyte: 0.05 M Tartaric acid + 0.05 M Triethanolamine. Dissolve 7.50 g Tartaric acid and 7.46 g Triethanolamine in 1 L DIW. Keep closed and prepare fresh when needed. Microorganismic growth can be observed in the solution after about a week. Although this growth does not appear to interfere with the analysis, the reagent should be discarded if growth is noticed.

6.2.3. Mercury, triple-distilled.

6.3. Precautions

6.3.1. Clean all glassware with a 10% HNO_3 solution and rinse several times with DIW. Air dry prior to use.

6.3.2. Wear gloves when handling soluble uranium compounds. Danger from radioactivity is minimal, but the soluble compounds are themselves toxic.

6.3.3. Mercury wastes can be temporarily placed in a beaker inside a fume hood that is left on. Permanent storage requires that the waste be placed in a securely closed metal container provided for that purpose.

6.3.4. Promptly clean up any spill of uranium solution that occurs by wiping it up with absorbent paper.

6.3.5. Remove any visible mercury drops that appear by auctioning with the vacuum hose provided for that purpose.

6.4. Sample preparation

6.4.1. Remove FWS-B filter from cassette and place in 125 mL Phillips beaker. Add 5 mL aliquot of electrolyte and extract for 30 minutes, with occasional swirling.

6.4.2. Transfer electrolyte to 25 mL volumetric flask. Rinse beaker with two more 5 mL aliquots of electrolyte and transfer these to volumetric flask. Bring flask to volume with electrolyte.

6.5. Standard Preparation

6.5.1. Standards in the range 0.5 - 10.0 µg should normally be analyzed. For a 10 mL cell volume, this corresponds to a concentration range of 0.05 - 1.0 ppm.

6.5.2. Prepare stock standards of 1.0, 10, and 100 ppm U by serial dilution of the 1000 ppm stock solution using DIW. Standards can be kept for six months.

6.5.3. Using calibrated pipettes, add appropriate aliquots of the stock standards to polarographic cells and bring to 10 ML volume with electrolyte solution as shown:

Stock Std. (µg/mL)	U Aliquot (µL)	Electrolyte (mL)	Final U Quantity in Cell (µg)
1.0	500	9.50	0.5
10	100	9.90	1.0
10	200	9.80	2.0
10	500	9.50	5.0
100	100	9.90	10.0

6.6. Analysis

6.6.1. Turn on the polarographic analyzer, 384-B, and allow it to warm up for about 45 minutes. Prior to analysis, turn on the digital plotter and prepare it with pen and paper.

6.6.2. The necessary parameters for analyzing soluble uranium by DPCSP have been entered into the memory of the 384-B. Recall the method number which analyzes soluble uranium and check the parameters to see that they correspond to the following conditions:

Analytical Technique:	Differential Pulse Stripping (DPS)
Initial Potential:	Approx. -0.050 V
Final Potential:	Approx. -0.330 V
Scan Rate:	2 mV/sec
Replications:	1
Pulse Height:	0.1 V
Purge Time:	90 sec
Equilibrium Time:	5 sec

6.6.3. The half-wave potential for uranium (VI) in this electrolyte (pH=3.5) is approx. -0.2 V vs. a Saturated Calomel Electrode (SCE). The actual peak voltage may differ a little from this value depending upon the condition of the reference electrode used.

6.6.4. Analyze the reagent blank and several standards before analyzing samples. Analyze a standard after every five or six samples.

6.6.5. Check the pH of each sample with pH paper before analyzing it. If the pH of the sample differs by > 0.2 pH units from the reagent blank, add small quantities of acid (HNO_3) or base (NaOH) until the pH of the sample is the same as the reagent blank.

6.6.6. Record the peak current (nA) and voltage of the peak (V) for each standard and sample. A form is provided for this purpose.

6.6.7. If non-uranium peaks occur or if the uranium peak shows signs of broadening, interferences should be suspected (4.2.2) and the sample should be analyzed by ICP or AA to determine the possibility and/or extent of the interference.

6.6.8. Plot a calibration curve of peak current (nA) vs. amount of standard (μg).

6.7. Calculations

6.7.1. Use the Colorimetric program or equivalent to plot a calibration curve (6.6.8).

6.7.2. Blank correct each air sample and wipe.

6.7.3. The concentration of soluble uranium in the sampled air is expressed as mg/m^3.

$$U \ (mg/m^3) = \frac{total \ ug \ U \ (blank \ corrected)}{air \ volume}$$

7. References

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