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⟨291⟩ SELENIUM

Add the following:

▲INTRODUCTION

This chapter describes three analytical procedures for the evaluation of the levels of selenium (Se). Use *Procedure 1*, *Procedure 2*, or *Procedure 3* as indicated in the individual monograph. *Procedure 2* or *Procedure 3* can be used in all circumstances, provided that suitability is demonstrated by meeting the *Requirements For Procedure Validation*.▲ (Official 1-Jun-2023)

Change to read:

▲PROCEDURES

• **Procedure 1: Spectroscopy**▲ (Official 1-Jun-2023)

Stock solution: Dissolve 40.0 mg of metallic selenium in 100 mL of dilute nitric acid (1 in 2) in a 1000-mL volumetric flask, warming gently on a steam bath if necessary to effect solution, add water to volume, and mix. Pipet 5 mL of this solution into a 200-mL volumetric flask, add water to volume, and mix. Each milliliter of the resulting solution contains the equivalent of 1 µg of selenium.

Diaminonaphthalene solution: Dissolve 100 mg of 2,3-diaminonaphthalene and 500 mg of hydroxylamine hydrochloride in 0.1 N hydrochloric acid to make 100 mL. Prepare this solution fresh on the day of use.

Standard solution: Pipet 6 mL of *Stock solution* into a 150-mL beaker, and add 25 mL of dilute nitric acid (1 in 30) and 25 mL of water.

Test solution: Clean combustion of the test material is an important factor in conducting the test. For compounds that burn poorly and produce soot, the addition of magnesium oxide usually results in more thorough combustion and reduces soot formation. Where the need to add magnesium oxide has been identified, it is specified in the individual monograph. Using a 1000-mL combustion flask and using 25 mL of dilute nitric acid (1 in 30) as the absorbing liquid, proceed as directed in *Oxygen Flask Combustion* ⟨471⟩, using a test specimen weighing 100–200 mg, unless directed otherwise in the individual monograph. Upon completion of the combustion, place a few milliliters of water in the cup, loosen the stopper, and rinse the stopper, the specimen holder, and the sides of the flask with about 10 mL of water. Transfer the solution with the aid of about 20 mL of water to a 150-mL beaker, and heat gently to the boiling temperature. Boil for 10 min, and allow the solution to cool to room temperature.

▲Analysis:▲ (Official 1-Jun-2023) Treat the *Standard solution*, the *Test solution*, and the reagent blank consisting of 25 mL of dilute nitric acid (1 in 30) and 25 mL of water, concomitantly and in parallel, as follows. Add ammonium hydroxide solution (1 in 2) to adjust to a pH of 2.0 ± 0.2. Dilute with water to 60 mL, and transfer to a low-actinic separator with the aid of 10 mL of water, adding the 10 mL of rinsings to the separator. Add 200 mg of hydroxylamine hydrochloride, swirl to dissolve, immediately add 5.0 mL of *Diaminonaphthalene solution*, insert the stopper, and swirl to mix. Allow the solution to stand at room temperature for 100 min. Add 5.0 mL of cyclohexane, shake vigorously for 2 min, and allow the layers to separate. Discard the aqueous layer, and centrifuge the cyclohexane extract to remove any dispersed water. Determine the absorbances of the cyclohexane extracts of the *Test solution* and the *Standard solution* in a 1-cm cell at the wavelength of maximum absorbance at about 380 nm, with a suitable spectrophotometer, using the cyclohexane extract of the reagent blank as the blank, and compare the absorbances: the absorbance of the *Test solution* is not greater than that of the *Standard solution* where a 200-mg test specimen has been taken, or is not greater than one-half that of the *Standard solution* where a 100-mg test specimen has been taken.

• **▲Procedure 2 and Procedure 3**

Both *Procedure 2* and *Procedure 3* are ICP-based procedures and can be used for the determination of selenium. *Procedure 2* can be used for the determination of selenium by inductively coupled plasma atomic (or optical) emission spectroscopy (ICP–AES or ICP–OES). *Procedure 3* can be used for the determination of selenium by ICP–MS.

Before initial use, the analyst should verify that the procedure is appropriate for the instrument and sample used (procedural verification) by meeting the *Requirements for Procedure Validation*.

Where a monograph specifies a limit for selenium concentration, the value listed in the monograph should be used as the *J* value for the purposes of this test.

System standardization and suitability evaluation using applicable reference materials should be performed on the day of analysis.

Sample preparation: Forms of sample preparation include neat, direct aqueous solution, direct organic solution, and indirect solution. The selection of the appropriate sample preparation depends on the material under test and is the responsibility of the analyst. When a sample preparation is not indicated in the monograph, an analyst may use any appropriately validated preparation procedure. In cases where

spiking of a material under test is necessary to provide an acceptable signal intensity, the blank should be spiked with selenium using, where possible, the same spiking solution. [Note—All liquid samples should be weighed.]

Closed vessel digestion: This sample preparation procedure is designed for samples that must be digested in a concentrated acid using a closed vessel digestion apparatus. Closed vessel digestion minimizes the loss of volatile impurities. The choice of a concentrated acid depends on the sample matrix. The use of any of the concentrated acids may be appropriate, but each introduces inherent safety risks. Therefore, appropriate safety precautions should be used at all times. [Note—Weights and volumes provided may be adjusted to meet the requirements of the digestion apparatus used.]

An example procedure that has been shown to have broad applicability is as follows. Dehydrate and predigest 0.5 g of primary sample in 5 mL of freshly prepared concentrated acid. Allow to sit loosely covered for 30 min in a fume hood. Add an additional 10 mL of concentrated acid, and digest using a closed vessel technique until digestion or extraction is complete. Repeat, if necessary, by adding an additional 5 mL of concentrated acid. [Note—Follow the manufacturer's recommended procedures to ensure safe use.]

Reagents: All reagents used for the preparation of sample and standard solutions should be free of elemental impurities, in accordance with *Plasma Spectrochemistry* ⟨730⟩.

Procedure 2: ICP–OES

Standardization solution 1: 1.5*J* of selenium in a matched matrix

Standardization solution 2: 0.5*J* of selenium in a matched matrix

Sample stock solution: Prepare as directed in *Sample preparation*. Allow the sample to cool, if necessary.

Sample solution: Dilute the *Sample stock solution* with an appropriate solvent to obtain a final selenium concentration of not more than 1.5*J*.

Blank: Matched matrix

Elemental spectrometric system

(See ⟨730⟩.)

Rinse: Use diluent.

Standardization: *Standardization solution 1*, *Standardization solution 2*, and *Blank*

System suitability

Sample: *Standardization solution 1*

Suitability requirements

Drift: Compare results obtained from *Standardization solution 1* before and after the analysis of the *Sample solution.*

Suitability criteria: NMT 20% for selenium. [Note—If samples are high in mineral content, rinse the system well before introducing the *Sample* in order to minimize carryover.]

Analysis: Analyze according to the manufacturer's suggestions for program and wavelength. Calculate and report results on the basis of the original sample size. [Note—Appropriate measures must be taken to correct for matrix-induced interferences (e.g., wavelength overlaps).]

Procedure 3: ICP–MS

Follow *Procedure 2* except for *Detector* and *Analysis*.

[Note—An instrument with a cooled spray chamber is recommended. (A collision cell or reaction cell may also be beneficial.)]

Detector: Mass spectrometer

Analysis: Analyze according to the manufacturer's suggestions for program and mass-to-charge ratio. Calculate and report results based on the original sample size. [Note—Appropriate measures must be taken to correct for matrix-induced interferences.]▲ (Official 1-Jun-2023)

Add the following:

▲REQUIREMENTS FOR PROCEDURE VALIDATION

The following section defines the validation parameters and the acceptance criteria for performance-based procedures. Meeting these requirements must be demonstrated experimentally using an appropriate system suitability procedure and reference materials. Any alternative procedure (e.g., an atomic-absorption-based procedure) that has been validated and meets the acceptance criteria that follow is considered to be suitable for use.

Meeting these validation acceptance criteria is sufficient to demonstrate that the procedure will produce comparable results to those obtained using the procedure prescribed in the monograph.

• **Accuracy**

Standard solutions: Prepare solutions containing selenium at concentrations ranging from 50% to 150% of *J* using appropriate reference materials.

Test samples: Spike the material under test with the appropriate reference materials before any sample preparation steps (digestion or solubilization). Prepare three replicate samples at concentrations ranging from 50% to 150% of *J* for selenium.

Acceptance criteria

Spike recovery: 70%–150% for the mean of three replicate preparations at each concentration

• **Precision**

Repeatability

Test samples: Six independent samples of material under test (taken from the same lot) spiked with appropriate reference materials for selenium at the indicated concentration

Acceptance criteria

Relative standard deviation: Not more than 20% (*N* = 6) for selenium

Intermediate precision (ruggedness)

Analysis: Perform the *Repeatability* analysis again on a different day, with different instrumentation, with a different analyst, or a combination thereof. Combine the results of this analysis with the first *Repeatability* analysis so the total number of analyses is 12.

Acceptance criteria

Relative standard deviation: Not more than 25% (*N* = 12) for selenium

- **Specificity:** The procedure must be able to unequivocally assess (see *Validation of Compendial Procedures* ⟨1225⟩) selenium in the presence of components that may be expected to be present, including matrix components.

- **Limit of Quantitation, Range, and Linearity:** Demonstrated by meeting the *Accuracy* requirement.▲ (Official 1-Jun-2023)

Add the following:

▲GLOSSARY

Concentrated acid: Concentrated ultra-pure nitric, sulfuric, hydrochloric, or hydrofluoric acid or aqua regia.

Aqua regia: Aqua regia is a mixture of concentrated hydrochloric and nitric acids, typically at ratios of 3:1 or 4:1.

Matched matrix: Solutions having the same solvent composition as the *Sample solution*. In the case of an aqueous solution, a matched matrix would indicate that the same acids and acid concentrations are used in both preparations.

Target limit or target concentration: The acceptance value for the elemental impurity being evaluated, in this case selenium. Where a monograph specifies a threshold limit, this shall become the target limit or target concentration of selenium for the material. Exceeding the target limit indicates that a material under test exceeds the acceptable value. The determination of compliance is addressed in other chapters.

***J*:** The concentration (w/w) of the element of interest, in this case selenium, at the target limit, appropriately diluted to the working range of the instrument.

Appropriate reference materials: Where "appropriate reference materials" are specified in the chapter, certified reference materials (CRMs) from a national metrology institute (NMI), or reference materials that are traceable to the CRM of an NMI should be used. An example of an NMI in the United States is the National Institute of Standards and Technology (NIST).▲ (Official 1-Jun-2023)

Auxiliary Information - Please check for your question in the FAQs before contacting USP.

Topic/Question	Contact	Expert Committee
<291> SELENIUM	Edmond Biba Senior Scientific Liaison	GCCA2020 General Chapters - Chemical Analysis 2020

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