Chemistry Lab USATHAMA METHOD KN01

Point of Contact: Marianne Walsh 603-646-4466.
USACRREL, Hanover, NH 03755

APPENDIX A: METHOD DOCUMENTATION IN USATHAMA (1990) FORMAT
ANALYTICAL METHOD FOR WHITE PHOSPHORUS IN SOIL OR SEDIMENT
(KN01) Revised April 92

I. SUMMARY

Analyte
This method is suitable for determining white phosphorus (P_4).

Matrix
This method is suitable for determining white phosphorus (P_4) in wet soil or sediment.

General method
A 40-g subsample of wet soil or sediment is placed into a 120-mL vial containing 10.0 mL of isooctane and 10.0 mL of degassed water. The sample is vortex-mixed for 1 min, then placed horizontally on a platform shaker for 18 hr or overnight. The sample is then allowed to stand vertically for 15 min to allow phase separation. A 1.0-µL aliquot of the isooctane layer is analyzed on a gas chromatograph equipped with a nitrogen-phosphorus detector.

II. APPLICATION

Tested concentration range
This method was tested over the range of concentration 0.000845–0.0169 µg/g.

Sensitivity
The instrumental response at the calculated reporting limit was 1700 peak height units for 3.38 picograms.

Reporting limit
The certified reporting limit was calculated to be 0.000881 µg/g.

Interferences
No interferences were found.

Analysis rate
In an 8-hr day, approximately 50 samples can be processed and analyzed.

Safety Information

White phosphorus is highly toxic and may ignite at 30°C if exposed to air. Procedures requiring the use of the solid material, such as the preparation of a stock solution, should be performed only in an inert atmosphere such as a nitrogen-purged glove bag. Skin contact with potentially contaminated soil should be avoided. Isooctane is a flammable organic solvent. Normal laboratory safety precautions should be followed.

III. APPARATUS AND CHEMICALS

Glassware/hardware

1. Glass vials, 120-mL, equipped with Teflon-lined caps
2. Pipettes—10-mL, volumetric, glass
3. Glove box or inflatable glove bag
4. Injection syringe—Hamilton, gas tight, 10-µL
5. Glass vacuum apparatus (to degas water)
6. Tweezers
7. Razor blades

Instrumentation

1. Gas chromatograph equipped with a nitrogen-phosphorus detector (NPD), SRI 8610 or equivalent.
2. DB-1 column, 0.53 mm I.D. 15 m, 3.0-µm film thickness or equivalent.
3. Digital integrator—HP3396A or equivalent
4. Vortex mixer
5. Platform shaker
6. Analytical balance (±0.1 mg)

Analyte

White phosphorus (P_4)

Chemical Abstract Service # [7723-14-0]

Density: 1.8 g/cm^3

Water solubility (15°C): 2.4 mg/L

Melting point: 44°C

Vapor pressure (20°C): 0.026 mm Hg

Octanol/water partition coefficient: 1200

Reagents

White phosphorus (99+%), Aldrich Chemical Co., no. 30,255-4
Isooctane (2,2,4-trimethylpentane), A.C.S. spectrophotometric grade
Water—Reagent grade
Nitrogen—pre-purified (for glove bag)
Nitrogen—zero grade (for GC carrier gas)
Hydrogen—zero grade (for NPD flame)

IV. CALIBRATION

Initial Calibration

Preparation of standards

The stock solution is prepared in a nitrogen-purged glove bag. The white phosphorus available from Aldrich Chemical Co. is a stick that is stored under water, and it generally has a white oxidized coat. A razor blade is used to slice a small piece (approx. 90 mg) off the stick of white phosphorus. Then the razor blade is used to remove the white oxidized coating. The piece of white phosphorus should be lustrous in appearance on all surfaces. The piece is dried under a gentle stream of nitrogen; since white phosphorus is hydrophobic, it sheds water immediately. The piece is placed with tweezers in a preweighed 250-mL volumetric flask containing a small amount of isooctane. The mass of white phosphorus is determined by difference. The flask is brought to volume with isooctane, and shaken until the white phosphorus dissolves. (To protect the stock solution from light, the flask is wrapped in aluminum foil). This stock solution has a concentration of approximately 360 mg/L.

A working stock solution is prepared by pipetting 1.00 mL of the stock solution into a 100-mL volumetric flask, and bringing the flask to volume with isooctane. The working stock solution has a concentration of approximately 3.6 mg/L.

To prepare calibration standards, 2.00 mL of the working stock solution is placed in a 100-mL volumetric flask and the flask brought to volume with isooctane. The resulting solution will have a concentration of 72.0 µg/L and serves as the 10XTRL standard. Solutions corresponding to 0.5X, 1.0X and 2XTRL are prepared in 100-mL volumetric flasks with 5.00, 10.0 and 20.0 mL of the 10XTRL standard. The solutions have concentrations of approximately 3.60, 7.20, and 14.4 µg/L. A solution corresponding to 5XTRL is prepared with 25.0 mL of the 10XTRL in a 50-mL volumetric flask and has a concentration of approximately 36.0 µg/L. Assuming a 40.0-g soil subsample is extracted with 10 mL of solvent, the concentration range for the calibration standards is equivalent to 0.0009-0.018 µg/g. Stock solutions and calibration standards are stored at 4°C in the dark.

Instrument calibration

Duplicate 1.0-µL aliquots of each standard are injected into the GC in random order. Peak heights or areas are obtained on the digital integrator.

Analysis of calibration data

The acceptability of a linear model with zero intercept is assessed using the protocol specified in USATHAMA QA program (January 1990). Based on the precertification calibration curve, a linear model with zero intercept is appropriate. Therefore, the slope of the best-fit regression line is equivalent to a response factor that can be compared with values obtained from replicate analyses of a single standard each day.

Daily calibration

The 72.0 µg/L (10XTRL) standard is used for daily calibration. This standard is analyzed in triplicate at the beginning of the analysis, singly after each ten samples and singly after the last sample of the day. A response factor is obained from the mean peak height obtained over the course of the day and compared with the response factor obtained for initial calibration. These values must agree within ±25% for the first seven days following the initial calibration and on subsequent days must be within ±2 standard deviations of a new initial calibration must be obtained. The response is expected to decline with operating time of the thermionic source in the nitrogen-phosphorus detector. The rate of decline depends on operating conditions.

V. CERTIFICATION TESTING

Preparation of spiking solutions

A stock white phosphorus spiking solution (360 mg/L) and a working stock solution (3.60 mg/L) are prepared in an identical manner to that described for the stock calibration standard and working stock solution.

The 10XTRL spiking solution is prepared by pipetting 20.0 mL of the 3.60-mg/L working stock solution into a 100-mL volumetric flask and bringing the flask to volume with isooctane. The resulting solution will have a concentration of 720 µg/L and serves as the 10XTRL spiking solution. Spiking solutions corresponding to 0.5X, 1.0X and 2XTRL are prepared in 100-mL volumetric flasks with 5.00, 10.0 and 20.0 mL of the 10XTRL spiking solution. The solutions have concentrations of approximately 36.0, 72.0, and 144 µg/L. A solution corresponding to 5XTRL is prepared with 25.0 mL of the 10XTRL in a 50-mL volumetric flask and has a concentration of approximately 360 µg/L.

Preparation of control spikes

Spiked soil samples are prepared by placing 40.0-g subsamples of prewetted USATHAMA Standard Soil in individual 120-mL glass vials. Each sample is spiked with 1.00 mL of one of the spiking standards and extracted as described below for real samples (except that 9.00 mL of isooctane is used for extraction). Samples are extracted immediately after spiking.

Analysis of soil spikes

Soil spikes are analyzed as described below for real samples.

VI. SAMPLE HANDLING AND STORAGE

All soil samples are stored in tightly sealed glass jars at 4°C in the dark until extracted. Contact with atmospheric oxygen should be a brief as possible since the white phosphorus will oxidize forming phosphoric acid. Sample handling is best performed in a nitrogen-purged glove bag inside a fume hood. Samples containing high

concentrations of white phosphorus can be immediately identified by a garlic-like odor and the formation of a cloud of vapor if the sample is exposed to the atmosphere.

VII. PROCEDURE

Soil extraction

A 40-g soil subsample is placed into a 120-mL vial containing 10.0 mL of isooctane and 10.0 mL of degassed water. This added water prevents the soil from forming a pellet during the shaking process. The samples are vortex-mixed for 1 min then placed horizontally on a platform shaker for 18 hr or overnight at 2500 rpm. Samples are allowed to stand vertically for 15 min to allow phase separation, then the isooctane layer is analyzed. If an isooctane layer fails to form, a portion of the sample is centrifuged for 5 min at 2500 rpm.

Determination

A 1.0-µL aliquot of the isooctane soil extract is injected on-column into the gas chromatograph equipped with a nitrogen-phosphorus detector. The GC column is maintained at 80°C. The carrier gas is nitrogen set at 30 mL/min. Under these conditions, white phosphorus elutes at 2 min.

VIII. CALCULATIONS

Response factor

Since a linear calibration curve with zero intercept is to be expected, calculation of results on a daily basis is obtained using a response factor. The mean response (R) for the white phosphorus standard is obtained in peak height units. The response factor RF is obtained by dividing the mean response by the known solution concentration (C) in units of µg/L:

$$RF = R/C$$

Analyte concentrations

Solution concentrations (µg/L) in the extracts (C_x) are obtained by dividing the response obtained for each sample (R_x) by the response factor

$$C_x = R_x/RF$$

Concentration in soil (X_x) on a µg/g or µg/kg basis is obtained by multiplying extract concentrations by the volume of extraction solvent (0.01 L), and dividing by the actual mass of wet soil.

IX. DAILY QUALITY CONTROL

Control spikes

Spiked soil samples are prepared as described for Class I methods in the USATHAMA QA Manual (January 1990). For each analytical lot, a method blank, a single spike at two times the certified reporting limit and duplicate spikes at ten times the certified reporting limit are analyzed. Control spikes are prepared using the appropriate spiking solution in a manner identical to that described in section V.

Control charts

The control charts required are described for Class I methods in USATHAMA QA Manual (January 1990). Standard Shewhart X and R chart for the duplicate high spikes and moving average X and R charts for the single low spike are required. Details on the charting procedures are specified in USATHAMA QA Manual (January 1990).

X. REFERENCES

USATHAMA (1990) U.S. Army Toxic and Hazardous Materials Agency Installation Restoration Quality Assurance Program. Aberdeen Proving Ground, Maryland.