$C_{20}H_{28}O_3$ to $C_{22}H_{30}O_5$ (Table 1) MW: 316.4 to 372.4 (active constituents) CAS: 8003-34-7 RTECS: UR4200000

METHOD: 5008, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3; Group II pesticide
ACGIH: 5 mg/m^3

PROPERTIES: viscous brown resin or solid; VP not significant

SYNONYMS: Active constituents include pyrethrin I and II, jasmolin I and II, and cinerin I and II.

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (glass fiber)	**TECHNIQUE:**	HPLC, UV DETECTION
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	six active constituents of pyrethrum
VOL-MIN:	20 L	**EXTRACTION:**	10 mL acetonitrile; stand 30 min
-MAX:	400 L		
SHIPMENT:	routine; ship bulk sample separately	**INJECTION VOLUME:**	25 µL
SAMPLE STABILITY:	at least 1 week @ 25 °C [1]	**COLUMN:**	C_{18} reverse phase, 10-µm packing, 25 to 30 cm
FIELD BLANKS:	2 to 10 field blanks per set	**MOBILE PHASE:**	85% acetonitrile/15% water, isocratic, 1.0 mL/min, room temperature, 2800 kPa (400 psi)
ACCURACY		**DETECTOR:**	UV absorption @ 225 nm
RANGE STUDIED:	1.4 to 8.5 mg/m^3 [1] (132-L samples)	**CALIBRATION:**	solutions of pyrethrum in acetonitrile
BIAS:	- 4.5%	**RANGE:**	0.1 to 1.8 mg per sample
OVERALL PRECISION ($\hat{S}_{rT}$):	0.070 [1]	**ESTIMATED LOD:**	0.01 mg per sample
ACCURACY:	± 13.8%	**PRECISION ($\hat{S}_r$):**	0.040 [1]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample.

INTERFERENCES: Specific interferences have not been studied. Mass spectrometry or gas-liquid chromatography with electron-capture detection may be needed for confirmation [1].

OTHER METHODS: This method is S298 [2] in a revised format. For bulk samples, gas-liquid chromatography with electron-capture detection has been recommended [3]. A modified HPLC method (C_8 column, programmed methanol/water or acetonitrile, isocratic) has been used [4].

REAGENTS:

1. Pyrethrum*, analytical standard solution(McLaughlin Gormley King Co., Minneapolis, MN; Chem Service, Inc., West Chester, PA; or other supplier).
   NOTE: Store away from direct light. Active constituents of pyrethrum oxidize in air and photo-decompose.
2. Acetonitrile, HPLC grade.*
3. Water, HPLC grade.
4. Isopropanol.
5. Calibration stock solution,* 60 mg/mL, in isopropanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm glass fiber filter and cellulose backup pad in filter holder held together with tape or shrinkable band.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with UV absorption detector at 225 nm, integrator and column (page 5008-1).
4. Ointment jars, 2-oz, squat form, with PTFE-lined screw caps.
5. Tweezers.
6. Pipet, TD, 10-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.
8. Syringe, 10-mL, with syringe filter.
9. Syringes or pipets, 5- to 100-µL.

SPECIAL PRECAUTIONS: Acetonitrile and pyrethrum solutions are toxic and flammable. Use gloves, goggles and other appropriate equipment to prevent eye contact or repeated and prolonged skin contact [5]. Wash skin and change clothes if contact occurs. Use in fume hoods and away from ignition sources.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 20 to 400 L.

SAMPLE PREPARATION:

3. Transfer the filter carefully to an ointment jar using tweezers.
4. Add 10.0 mL acetonitrile. Seal and gently swirl the jar to wet the filter. Let stand 30 min with occasional swirling.
5. Filter the sample solution through a syringe filter.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 0.01 to 1.8 mg pyrethrum per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with the samples and blanks (steps 9, 10 and 11).
   c. Prepare calibration graph (peak area vs. mg pyrethrum/10 mL).
7. Determine recovery (R) at least once for each batch of filters used for sampling in the range of the samples. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of calibration stock solution, or a dilution thereof, onto the filters. Allow filters to air-dry.
   b. Store samples overnight in ointment jars.

c. Prepare (steps 4 and 5) and analyze together with working standards (steps 9 through 11).
d. Prepare a graph of R vs. mg pyrethrum recovered.

8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

9. Set HPLC system according to manufacturer's recommendations and to conditions on page 5008-1.
10. Inject sample aliquot using syringe, fixed volume sample loop, or autosampler.
11. Measure peak area.

NOTE: Pyrethrum is a mixture of at least six components which elute in two major peaks (t_r = 5 to 7 min under these conditions). The minor peaks have been shown by mass spectrometry not to be pyrethrums. The components may be separated by gas chromatography [1,4].

CALCULATIONS:

12. Determine the mass, mg (corrected for R) of pyrethrum found in the sample (W) and in the average media blank (B) from the calibration graph.
13. Calculate concentration, C, of pyrethrum in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S298 [2] was issued on August 3, 1979, and validated over the range 1.4 to 8.5 mg/m^3 using atmospheres generated from Premium Pyrocide 175 (McLaughlin Gormley King Co.) [1]. Standards and collected filter samples were analyzed by GC/MS. Lab testing was done with spiked filters and atmospheres dynamically generated by atomization of a hydrocarbon solution; verified by PTFE filter/isooctane bubbler analyzed by gas chromatography with electron capture detector (absence of pyrethrum in the bubbler was established by mass spectrometry). Samples containing 0.7 mg pyrethrum collected from a test atmosphere were stable for seven days at ambient conditions (average recovery = 98.2%). Collection efficiency = 99.7% for 120-L samples collected at 1 L/min at 9 mg/m^3. Precision and accuracy are given on page 5008-1.

REFERENCES:

[1] Backup Data Report, S298 (NIOSH, unpublished, August 3, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S298, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] Changes in Official Methods of Analysis, J. Assoc. Off. Anal. Chem., 65, 455-456 (1982).
[4] UBTL, Inc., NIOSH Sequence Reports 3481-J (unpublished, August 30, 1982) and 4151-J (unpublished, November 3, 1983).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

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Table 1. Active constituents of Pyrethrum.

Compound	Formula	M.W.	CAS #
Cinerin I	$C_{20}H_{28}O_3$	316.44	25402-06-6
Cinerin II	$C_{21}H_{28}O_5$	260.45	
Jasmolin I	$C_{21}H_{30}O_3$	330.47	
Jasmolin II	$C_{22}H_{30}O_5$	374.48	
Pyrethrin I	$C_{21}H_{28}O_3$	328.45	121-21-1
Pyrethrin II	$C_{22}H_{28}O_5$	372.46	121-29-9