USATHAMA METHOD AAA9
ISOPROPYLMETHYL PHOSPHONIC ACID, METHYL PHOSPHONIC ACID, AND FLUOROACETIC ACID IN SOIL

I. SUMMARY

A. ANALYTES

This method is applicable for the quantitative analysis of isopropylmethyl phosphonic acid (IMPA), methyl phosphonic acid (MPA), and fluoroacetic acid (FC2A) in soil by ion chromatography. Note: IMPA and ethyl methyl phosphonic acid (EMPA) coelute. This method was certified using IMPA only, however, reported data could include total IMPA and EMPA.

B. MATRIX

This method is applicable to most soils and sediments. Sample extracts with specific conductivities over 800 microSiemens per centimeter (uS/cm) need dilution to prevent column over-loading. (This is not common with soil extracts.)

C. GENERAL METHOD

A two gram portion of a sample is shaken on a mechanical shaker with 20 mL of deionized water for 30 min. The mixture is centrifuged before analyzing. A protion of the extract is passed through 20 um frit in the autosampler vial to a 50 uL injection loop. The 50 uL of sample is injected into a 1.0 mL/min flowstream of a 0.75 mM NaOH eluent with 1.5% methanol. The sample passes through a guard column and then through an anion separator column which retains the anions for a characteristic retention time. The 0.75 mM NaOH eluent is programed to run for 6.9 minutes following sample injection. A second eluent (48 mM NaOH with 1.5% methanol) is then linearly programmed for 17 minutes to replace eluent 1 to a final eluent concentration of 48 mM NaOH (100% eluent 2). Characteristic retention times are used for compound identification and results are calculated from linear calibration curves.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration range for IMPA, FC2A, and MPA is 2.0 to 40 micrograms per gram (ug/g).

B. SENSITIVITY

The approximate peak areas in microvolts-minutes (uV-min) [with the conductivity detector on 10 microSiemens per volt (uS/V) scale] for 2 ug/g in standard soil is 50,000.

C. CERTIFIED REPORTING LIMITS

The certified reporting limits (CRL) in soil, calculated using the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) reporting limit program, is 2.11 ug/g for IMPA, 2.0 ug/g for FC2A and 2.0 ug/g foor MPA. The upper certified range (UCR) is 40 ug/g.

D. INTERFERENCES

A compound that coelutes with an analyte is an interference. Formic acid coelutes with fluoroacetic acid, and some natural soils have detectable concentrations of formic acid. EMPA coelutes with IMPA and this method can not distinguish the difference. Since EMPA is a byproduct for VX production and IMPA a byproduct of GB production, specific site investigations will not require differentiation unless both process had been used at a site. Carbonate elutes just after MPA and high concentrations can interfere with accurate determination of MPA. Samples with high specific conductivities (>800 uS/cm) i.e. high concentrations of anions can cause column over-loading, requiring the sample to be diluted. High concentrations of transition metals can cause low recovery for both IMPA and MPA.

E. ANALYSIS RATE

An autosampler can make 41 injections in a 24 hour period. This relates to the analysis of approximately 20 environmental samples with the remaining injections for calibration curves, daily control spikes reference samples, and continuing calibration samples.

F. SAFETY INFORMATION

Care should be taken when preparing or handling sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) reagents.

III. APPARATUS AND CHEMICALS

A. HARDWARE/GLASSWARE

1. Class A volumetric flasks (1000 mL, 100 mL, 50 mL);
2. Mechanical shaker;
3. Centrifuge;
4. Disposable plastic centrifuge tubes, 50 mL capacity;
5. Mechanical pipettes (50, 100, 500 and 1000 micro-liter [uL]).

B. INSTRUMENTATION

1. Ion chromatograph (Dionex Model 4000, with gradient analytical pump capabilities);
2. Guard Column (Dionex PAX-500 guard)
3. Anion separator column (Dionex PAX-500);
4. Anion membrane suppressor (Dionex AMMS-II);
5. Integrator (Maxima® integration system or equivalent), and
6. Anion trap column (Dionex ATC).

Parameters:

a. Eluents: (1) 0.75 millimolar (mM) and
(2) 48 mM sodium hydroxide.

b. Suppressor reagent: 40 mM sulfuric acid.

c. Flow rate and pressure: 1.0 mL/min at 750 pounds per square inch (psi) (typical).

d. Detector range: 30 uS full-scale.

e. Injection loop: 50 uL.

f. Gradient program: Enter the following program into the gradient-pump microprocessor:

Time	Eluent	Percent	Notes	Flow (mL/min)
0.0	1	100		1.0
0.1	1	100	(inject)	1.0
0.2	1	100	(inject off)	1.0
7.0	1	100	(gradient start)	1.0
24.0	2	100	(gradient stop)	1.0
24.1	1	100	(flush)	1.0

C. ANALYTES

The Chemical Abstract Service (CAS) Registry Numbers are:

Analyte	CAS Registry No.
IMPA	*
MPA	*
FC2A	62-74-8

* not available

D. REAGENTS AND SARMS

1. ASTM Type I grade deionized water (DIW).
2. Sodium hydroxide; 50% weight/weight, reagent grade.
3. Sulfuric acid (H_2SO_4); reagent grade [Baker, American Chemical Society (ACS)].
4. Standards [Standard Analytical Reference Materials (SARMs)]:

   IMPA (SARM Compound 1264);

   MPA (SARM Compound 1390);

   FC2A (Fluka Chemical Company, Lot 261038).
5. Methanol; reagent grade [Baker, ACS].
6. A 0.75 millimolar (mM) sodium hydroxide eluent (eluent No. 1) is prepared by adding 150 uL of 50% w/w sodium hydroxide to 4 liters (L) of DIW which has been degassed previously with helium for 5 min. Add 60 mL of methanol.
7. A 48 mM NaOH eluent (eluent No. 2) is prepared by adding 2.5 mL of 50% w/w NaOH to 1 L of degassed DIW. Add 15 mL of methanol.
8. Regenerant [approximately 40 millinormal (mN) sulfuric acid] is prepared by adding 4.5 mL of conc. sulfuric acid to 4 L of DIW.

Note: Eluents must be prepared with a minimum amount of carbonate contamination. Carbonate has a higher eluting strength than hydroxide and will give poor and non-reproducible results if allowed to contaminate eluents. A carbonate-free eluent stock must be used. Deionized water used to perpare NaOH and eluents must be degassed with helium prior to use and prepared eluents kept under helium to prevent adsorption of carbon dioxide from air.

IV. CALIBRATION

A. INITIAL CALIBRATION

1. Preparation of Calibration Standards.

   a. Prepare 4,000 ug/mL individual calibration stock solutions (ICSS) by weighing 200 mg of IMPA and MPA standard material, and 256.3 mg of sodium fluoroacetate into separate 50 mL volumetric flasks and diluting

each to volume with DIW. Prepare fresh at least semiannually and store at 4°C.

b. Prepare a 100 ug/mL combined calibration stock solution (CCSS) by adding 2.5 mL of each ICSS to a 100 mL volumetric flask and diluting to volume with DIW. Prepare fresh at least quarterly, and store at 4°C.

c. The working calibration standards are prepared fresh for each lot as follows:

Standard	Concentration (ug/L)	Volume (mL) of CCSS to 50 mL with DIW
Blank	0	0
A	100	0.05
B	200	0.1
C	400	0.2
D	1,000	0.5
E	2,000	1.0
F	4,000	2.0
G	6,000	3.0

Note: ug/L = micrograms per liter.

2. Instrument Calibration.

a. Establish a stable baseline with eluent No. 1 (0.75 mM sodium hydroxide) at 100 percent (20 to 30 min). Initiate at least two gradient runs prior to beginning analysis to equilibrate the system.

b. With integrator ready to receive trigger signal from ion chromatograph (due to narrow peak windows, manual start of integrator is not recommended), inject high standard (standard G - 6,000 ug/L).

c. Upon completion of Standard G run, test integration parameters for correct baseline placement and proper peak starts and peak ends.

d. Proceed with calibration standard run, from high to low, and a blank. Allow 35 min. between injections.

e. A reference standard, prepared independent of the calibration stock, is analyzed and must be within $\pm$ 10% of the true value. If the reference is not within $\pm$ 10% of the true value, it will be reanalyzed. If the reference is still outside of criteria, the reason must be determined and appropriate corrective action taken.

f. Analyze method blank and daily control spike samples.

3. Analysis of Calibration Data.

After analyzing the standards (i.e., one blank and eight standards), the data are tabulated and graphed. For precertification calibration, the duplicate calibration data are analyzed using the lack-of-fit (LOF) and zero-intercept (ZI) tests (USATHAMA QA Plan, January 1990). The three analytes passed LOF/ZI tests, therefore,

calibration curves are linear. Attachment 1 contains the precertification data.

4. Calibration Checks.

After every 12 samples and at the end of each day's analyses, the F Standard (4,000 ug/L) is reanalyzed. The reference standard is also reanalyzed at the end of each day's analyses. If the measured concentration for these standards is not ± 10% of the true value, the instrument is recalibrated and all samples since the last acceptable calibration check are reanalyzed. After seven runs, ± 2 standard deviations of the percent recovery will be evaluated as a criteria.

B. DAILY CALIBRATION

Daily calibration and initial calibration curve and QC checks will be performed as stated in Sec.IV.A.

V. CERTIFICATION TESTING

A. PREPARATION OF SPIKING SOLUTION

1. Individual Spike Stock Solutions (ISSS): Prepare separate 4,000 ug/mL stock standards (independent of stock calibration standards) as in Sec. IV.A.1. Prepare fresh at least semiannually and store at 4°C.
2. Combined Spike Stock Solution (CSSS): Prepare a 100 ug/mL combined intermediate spike solution by adding 2.5 mL of each control spike stock to a 100 mL volumetric flask and diluting to volume with DIW. Prepare fresh at least quarterly and store at 4°C.
3. Working Control Spike Solution (WCSS): Working control spike solutions are prepared as follows:

Control Spike	Concentration (ug/mL)	Volume (mL) of CICSS Diluted to 50 mL
A	0	0
B	4	2
C	8	4
D	16	8
E	40	20
F	80	40

B. PREPARATION OF CERTIFICATION CONTROL SPIKE SAMPLES

1. Weigh 2.00 g of USATHAMA standard soil into separate 50 mL disposable plastic centrifuge tubes. Add 1 mL of each of the working control spike solutions (A through F, Sec. V.A.3.) to each 2.0 ± 0.02g of standard soil sample as shown in this section. Let set for 1 hour before adding 20.0 mL of DIW. Shake for 30 min. and centrifuge for 20 min.

Spike Level	Spike Conc. (ug/g)	Concentration of WCCS added to Standard Soil
0X	0	0 (A)
0.5X	2	4 (B)
1X	4	8 (C)
2X	8	16 (D)
5X	20	40 (E)
10X	40	80 (F)

2. The control spike samples are prepared as specified in Sec. V.B.1 each day for four consecutive days and analyzed as described in Sec.VII.C. Attachment 2 contains the method certification data.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE AND PRESERVATION

Samples for IMPA, FC2A and MPA analysis should be collected in amber glass containers with minimum headspace. Samples must be maintained in a temperature-controlled room at 4 degrees Celsius (°C).

B. SAMPLING CONTAINERS

Samples are collected in amber-glass jars with teflon-lined lids (100 g volume is adequate).

C. STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4°C.

D. HOLDING TIME LIMITS

The holding time between sampling and extraction is seven days and 40 days from extration to analysis.

E. SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. The CSSS spiking stock solution should be verified within at least seven days prior to use. Verification can be accomplished by running a separate dilution of the CSSS on the same day the samples are analyzed.

VII. PROCEDURE

Daily quality control spikes (see Sec.IX for preparation) and environmental samples are analyzed as follows:

A. SEPARATIONS

Weigh a 2.0 ± 0.02g sample into a 50 mL disposable plastic centrifuge tube. Add 20.0 mL of DIW and shake on a mechanical shaker for 30 min. Centrifuge for 20 min.

B. CHEMICAL REACTION

There are no chemical reactions.

C. INSTRUMENTAL ANALYSIS

1. Daily instrument calibration and QC checks are performed as described in Sec.IV.B. Instrument conditions are defined in Sec.III.B.
2. Eluent Preparations for Eluent 1, Eluent 2, and the regenerant are described in Section III.D.6-8.
3. Analysis should proceed in the following manner:
   a. Run calibration standards;
   b. Verify calibration with a reference;
   c. Analyze the daily control spikes and insure that they are in control;
   d. Analyze samples and continuing calibration checks;
   e. Dilute samples that exceed the upper certified range with DIW and reanalyze;
   f. Conclude the run with a blank, standard F, and a reference.

VIII. CALCULATIONS

Calculate the linear regression equation for response (peak area) versus concentration using the least-squares method. Using the linear regression equation, concentration for extract analytes in the following manner:

$$\text{Preliminary results (ug/g)} = \frac{\text{Solution Conc. (ug/L) x Extract Vol. (L) x Dilution Factor}}{\text{Sample Weight (g)}}$$

Data are submitted to the USATHAMA data management system on a wet weight basis with moisture data.

IX. DAILY QUALITY CONTROL

A. PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. Individual Spike Stock Solutions (ISSS): Prepare separate 4,000 ug/mL stock standards (independent of stock calibration standards) by weighing 200 mg of IMPA and MPA standard material, and 256.3 mg of sodium fluoroacetate into separate 50 mL volumetric flasks and diluting each to volume with DIW. Prepare fresh at least semiannually and store at 4°C.
2. Combined Spike Stock Solution (CSSS): Prepare a 100 ug/mL combined intermediate spike solution by adding 2.5 mL of each control spike stock to a 100 mL volumetric flask and diluting to volume with DIW. Prepare fresh at least quarterly and store at 4°C.
3. Spike stock solution verification can be accomplished by running a separate dilution of the CSSS on the same day the samples are analyzed.
4. With each daily lot of environmental samples, prepare the daily control spike samples as follows (as prepared in Sec. V.B.):

Daily Control Spike	Spike Concentration (ug/g)	Working Control Spike Solution (Sec. V.A.3.)
Blank	0	A
Low Spike	4	C
High Spike	20	E
High Spike	20	E

B. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

The found response is corrected for method blank response, when necessary, prior to calculation of the found concentration. Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot,
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot, and

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits are presented in Table I.

Table I: Initial Warning and Control Limits

METHOD: Ion Chromatography
COMPOUND: IMPA, MPA, FC2A - water
UNITS: UGL

3 PT. MOVING AVERAGE $\bar{X}$ - R

CONC. = 400

	UCL $\bar{X}$	UWL $\bar{X}$	= X	LWL $\bar{X}$	LCL $\bar{X}$	UCL R	UWL R	$\bar{R}$
IMPA	93.0	91.0	86.9	82.8	80.7	15.4	12.3	6.0
MPA	121.0	116.7	108.2	99.6	95.4	32.2	25.6	12.5
FC2A	105.4	101.4	93.5	85.6	81.7	29.9	23.8	11.6

SINGLE DAY $\bar{X}$ - R

CONC. = 2000

	UCL $\bar{X}$	UWL $\bar{X}$	= X	LWL $\bar{X}$	LCL $\bar{X}$	UCL R	UWL R	$\bar{R}$
IMPA	100.9	100.2	98.7	97.3	96.6	3.8	2.9	1.1
MPA	107.4	105.9	102.8	99.6	98.1	8.2	6.3	2.5
FC2A	102.5	101.8	100.4	99.0	98.3	3.6	2.8	1.1

X. REFERENCES

A. U.S. Army Toxic and Hazardous Materials Agency Quality Assurance Plan (January 1990).

B. Dionex Model 4000i Instrument operation Manual. The Practice of Ion Chromatography, Frank Smith, Jr., and Richard C. Chang.

XI. DATA

A. OFF-THE-SHELF-CHARACTERIZATION – Not required since stock solutions are USATHAMA SARMS.

B. PRECERTIFICATION CALIBRATION DATA --See attachment 1.

C. DAILY CALIBRATION FOR CERTIFICATION AND CERTIFICATION DATA. See attachment 2.

D. REFERENCE METHOD - none available.

E. EXAMPLE CHROMATOGRAM - see attachment 3.

F. LOT FOLDER ORGANIZATION INCLUDING METHOD SUMMARY - see attachment 4.