PMRMA METHOD LT03
AGENT BREAKDOWN PRODUCTS (IMPA,MPA,CLC2A) 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), fluoroacetic acid (FC2A),and chloroacetic acid (CLC2A) in soil by ion chromatography. Note: IMPA and ethyl methyl phosphonic acid (EMPA) coelute. Method performance documentation was certified using IMPA only, however, reported data hits for IMPA represent the total of IMPA and EMPA.

B. MATRIX

This method is applicable for the analysis of water leachable components in most soils and sediments. Sample leachate (extracts) with specific conductivities over 800 microSiemens per centimeter (uS/cm) need dilution to prevent column over-loading. An alternative procedure passes the leachate through a silver column to remove chloride, thereby lowering conductivity. (The conductivity problem is not common with normal 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 minutes. The leachate or extract is centrifuged and a portion of the extract can be passed through a silver-form cation resin cartridge followed by a 0.45 um polypropylene Whatman Puradisc filter and collected in a 7 ml vial to await analysis. The autosampler injects 100 uLs of the sample by an injection loop into a 1.0 mL/min flowstream of a 0.23 mM NaOH eluent. The sample passes through a guard column and then through an anion separator column which retains the anions for a characteristic retention time. The 0.23 mM NaOH eluent is programmed to run for 10.0 minutes following sample injection. A second eluent (48 mM NaOH) is then linearly programmed for 10 minutes to replace eluent 1 to a final eluent concentration of 9.8 mM NaOH (20% eluent 2). After which, a gradient step change to 28.8 mM for 2 minutes is enacted to flush the separator column of high retention anions (notably phosphate). Characteristic retention times are used for compound identification and results are calculated from quadratic calibration curves.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration range for IMPA, FC2A, CLC2A and MPA is 0.1 to 20 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 the 0.5 ug/g spike in standard soil (0.20 ug/g for FC2A) are:

ANALYTE	RESPONSE
IMPA	85,000
FC2A	65,000
CLC2A	115,000
MPA	2,000,000

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 and 2 days of control spikes, is 0.50 ug/g for IMPA, MPA, and CLC2A; and 0.182 ug/g for FC2A. The upper certified range (UCR) is 20 ug/g. The slopes for the two days of control spikes (0.1 ug/g -- 20 ug/g) compare favorably with the slopes from the original 4 days of control spikes (AAA9: 2 ug/g -- 40 ug/g). The table below compares the slopes presented as % recoveries for these two sets of certifications:

ANALYTE	SLOPE (0.1 -- 20 ug/g)	SLOPE (2 -- 40 ug/g)
IMPA	96.07	92.9
MPA	88.17	86.8
CLC2A	97.5	----
FC2A	100.3	92.9

D. INTERFERENCES

A compound that coelutes with an analyte is an interference. Formic acid coelutes just before fluoroacetic acid, and concentrations greater than 20 ug/g can be an interference. 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 processes had been used at a site. 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. High concentrations of chloride and carbonate cause peak shifts and broadening, but are effectively removed by passing the sample extracts through cation exchange resin in the silver form.

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]).
6. 50 ml syringe.
7. Silver-form cation resin cartridges (Alltech maxi-clean @ AG-IC or equivalent).
8. Whatman Puradisc polypropylene filters (0.45 um).
9. 7 mL polypropylene screw-cap vials for sample storage.

B. INSTRUMENTATION

1. Ion chromatograph (Dionex Model 4000, with gradient analytical pump capabilities);
2. Guard Column (Dionex AG 11 guard)
3. Anion separator column (Dionex AS11);
4. Anion membrane suppressor (Dionex AMMS-II or equivalent);
5. Integrator (Maxima® integration system or equivalent), and
6. Anion trap column (Dionex ATC).

Parameters:

a. Eluents: (1) 0.23 millimolar (mM) and
(2) 48 mM sodium hydroxide.

b. Suppressor reagent: 25 mM sulfuric acid.

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

d. Detector range: 10 uS full-scale.

e. Injection loop: 100 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
0.3	1	100	(inject off)	1.0
10.0	1	100	(gradient start)	1.0
21.0	2	20	(gradient stop)	1.0
21.1	1	60	(flush)	1.0
23.0	2	60	(flush)	1.0
23.1	1	100	Re-Equilibration	1.0

C. ANALYTES

The Chemical Abstract Service (CAS) Registry Numbers are:

Analyte	CAS Registry No.
IMPA	*
MPA	*
FC2A	62-74-8
CLC2A	*

* 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 (Aldrich);

   FC2A (Fluka Chemical Company).

   CLC2A (Aldrich PY 02914 LX).
5. A 0.23 millimolar (mM) sodium hydroxide eluent (eluent No. 1) is prepared by adding 48 uL of 50% w/w sodium hydroxide to 4 liters (L) of DIW which has been degassed previously with helium for 10 min.
6. 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.
7. Regenerant [approximately 25 millinormal (mN) sulfuric acid] is prepared by adding 7 mL of conc. sulfuric acid to 10 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 prepare 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. Glass eluent containers should be used, since CO2 can diffuse through the walls of plastic containers.

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, MPA and CLC2A 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
G	2000 ug/L	1.0
F	1000 ug/L	0.5

The low level standards are prepared by serial dilutions of the high level standards as follows:

E	400 ug/L	1: 5 of Standard G
D	100 ug/L	1:10 of Standard F
C	40 ug/L	1:10 of Standard E
B	20 ug/L	1: 5 of Standard D
A	10 ug/L	1: 4 of Standard C

* NOTE: Adhesion of the analytes to the walls of glassware will occur. All standards will be prepared using polypropylene volumetric labware. Also, plastic vials will be used in the autosampler (do not use glass vials).

2. Instrument Calibration.

a. Establish a stable baseline with eluent No. 1 (0.23 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 - 2,000 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 independently 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 will be determined and corrected (ie standards prepared or instrumental conditions changed). The calibration curve will then be reanalyzed.

f. Analyze method blank and daily control spike samples.

3. Analysis of Calibration Data.

After analyzing the replicate calibration standards, the data were tabulated and graphed to evaluate statistical linearity checks for lack-of-fit (LOF) and zero-intercept (ZI) tests (USATHAMA QA Plan, January 1990). The replicate calibration curves for the four analytes passed LOF/ZI tests and are therefore considered linear, however quadratic regressions are preferred in order to improve predictions of standards near the detection limit. 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 (1,000 ug/L) is reanalyzed. If the measured concentration for these standards is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable calibration check are reanalyzed. After seven runs, $\pm$ 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. METHOD PERFORMANCE 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:

Working Control Spike Solution	Concentration (ug/mL)	Volume (mL) of CSSS Diluted to 50 mL
DIW	0	0
WCSA	1.0	0.5
WCSB	10.0	5.0

B. PREPARATION OF METHOD PERFORMANCE CONTROL SPIKE SAMPLES

1. Weigh 2.00 ± 0.02g of USATHAMA standard soil into separate 50 mL disposable plastic centrifuge tubes. Add indicated amount of each of the appropriate spike solutions (Sec. V.A.2 and 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)	Volume (mL) of Spike Solution added to Standard Soil
0X	0	0 (DIW)
0.50X	0.10	0.2 (WCSA)
1.0X	0.20	0.4 (WCSA)
2.5X	0.50	0.1 (WCSB)
5.0X	1.0	0.2 (WCSB)
10X	2.0	0.4 (WCSB)
25X	5.0	0.1 (CSSS)
50X	10.0	0.2 (CSSS)
100X	20.0	0.4 (CSSS)

2. The control spike samples are prepared as specified in Sec. V.B.1 each day for two consecutive days and analyzed as described in Sec.VII.C. Two days were required rather than four days because the purpose of the method performance documentation was to extend the certified range of Method AAA9 for lower CRLs. 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 extraction 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 $\pm$ 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. Place 3 mL of extract into each syringe and aspirate to waste through a silver-form cation resin cartridge with a .45 u polypropylene Whatman filter attached to catch particles of resin which can escape from the cartridge. Place vials and vial holders under each aspiration setup and pour 7 mL of extract into each syringe and aspirate to completion. Collect the treated extract in 7 ml vials; stored at 4°C until analysis.

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

Preliminary results (ug/g)=

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

Data are submitted to the PMRMA data management system on a wet weight basis with moisture data. If the sample concentration is greater than the highest certified range, the sample will be diluted within the certified range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported.

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, MPA and CLC2A 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 High Spike Stock Solution (CHSSS): Prepare a 100 ug/mL combined intermediate spike solution by adding 2.5 mL of each 4000 ug/mL 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. Combined Low Spike Stock Solution (CLSSS): Prepare a combined intermediate spike solution, containing 10 ug/mL IMPA,MPA and CLC2A, and 4 ug/mL FC2A by adding 0.250 mL of each 4000 ug/mL IMPA,MPA and CLC2A control spike stock and 0.100 mL of 4000 ug/mL FC2A control spike stock to a 100 mL volumetric flask and diluting to volume with deionized water. Prepare fresh at least quarterly and store at 4°C.

4. Working Low and High Spike Solutions(WLSS and WHSS): Prepare separate 50 mL solutions for low level and high level control spiking. For the WLSS dilute 10 mL of CLSSS to a 50 mL final volume with water. For the WHSS dilute 15 mL of CHSSS to a 50 mL final volume with water. These solutions should be prepared monthly and stored at 4°C.

5. Spike stock solution verification can be accomplished by running a separate dilutions on the same day the samples are analyzed.

6. With each daily lot of environmental samples, prepare the daily control spike samples as follows by adding 1.0 mL of the appropriate solution (DIW, WLSS, or WHSS) to 2 g of standard soil and allow to stand for 1 hour:

Daily Control Spike	Spike Concentration (ug/g)	Working Control Spike Solution (Sec. V.A.3.)
Blank	0	DIW
Low Spike	1.0 (0.4 for FC2A)	WLSS
High Spike	15.0	WHSS
High Spike	15.0	WHSS

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.

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** -- Performed previously for AAA9 and LW18

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**