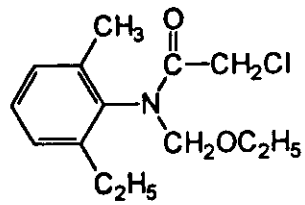
ACETOCHLOR : 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide.



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MULTIRESIDUE METHOD FOR THE ANALYSIS OF ACETOCHLOR AND OTHER ORGANOHALIDE PESTICIDES AND COMMERCIAL POLYCHLORINATED BIPHENYL (PCB) PRODUCTS IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY.

SCOPE

This method is applicable to the determination of acetochlor in tap (drinking) water and ground water to levels of 0.2 µg litre^{-1}. The method is based on EPA method 505 (Ref 1), Additionally, method 505 is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water:

Alachlor	Methoxychlor
Aldrin	cis-Nonachlor
Atrazine	trans-Nonachlor
Chlordane	Simazine
alpha-Chlorodane	Toxaphene
gamma-Chlorodane	Arochlor 1016
Dieldrin	Arochlor 1221
Endrin	Arochlor 1232
Heptachlor	Arochlor 1242
Heptachlor Epoxide	Arochlor 1248
Hexachlorobenzene	Arochlor 1254
Hexachlorocyclopentadiene	Arochlor 1260
Lindane	

PROCEDURE

APPARATUS

SAMPLE CONTAINERS - 40 - mL screw cap vials (Pierce #13075 or equivalent) each equipped with a size 24 cap with a flat, disc-like TFE facing backed with a polyethylene film/foam extrusion (Fisher #02-883-3F or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place the vials in a 400°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

VIALS - auto sampler, screw cap with septa, 1.8 mL, Varian #96-000099-00 or equivalent or any other autosampler vials not requiring more than 1.8 mL sample volumes.

AUTO SAMPLER - Hewlett-Packard 7671A, or equivalent.

MICRO SYRINGES - 10 and 100 µL.

MICRO SYRINGE - 25 µL with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.

PIPETTES - 2.0 and 5.0 mL transfer.

VOLUMETRIC FLASKS - 10 and 100 mL, glass stoppered.

STANDARD SOLUTION STORAGE CONTAINERS - 15-mL bottles with PTFE-lined screw caps.

GAS CHROMATOGRAPH - Analytical system complete with temperature programmable GC suitable and split/splitless injector for use with capillary columns and all required accessories including syringes, analytical columns, gases, a linearized electron capture detector and stripchart recorder. A data system is recommended for measuring peak areas.

Column - 0.32 mm ID x 30 M long fused silica capillary with chemically bonded methyl polysiloxane phase (DB-1, 1.0 µm film, or equivalent). Helium carrier gas flow is about 25 cm/sec linear velocity, measured at 180° with 9 psi column head pressure. The oven temperature is 50°C (1 min)-250°C at 40°C min^{-1} and held at 250°C for 10 minutes. Injector temperature : 200°C. Splitless Mode : 0.5 min. Detector temperature : 290 °C

Under these conditions the retention time for acetochlor is 8.1 minutes.

Sample chromatograms for acetochlor and other similar acetanilides alachlor and metolachlor are presented in Figures 1-7.

II **REAGENTS**

Hexane extraction solvent - UV Grade, Burdick and Jackson # 216 or equivalent.

Methyl alcohol - ACS Reagent Grade, demonstrated to be free of analytes.

Sodium chloride, NaCl - ACS Reagent Grade - For pre-treatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C and hold for 30 min. Place in a bottle and cap.

Sodium thiosulfate, $Na_2S_20_3$, ACS Reagent Grade - For preparation of solution (0.04 g/mL), mix 1 g of $Na_2S_20_3$ with reagent water and bring to 25-mL volume in a volumetric flask.

REAGENT WATER - Regent water is defined as water free of interference when employed in the procedure described herein.

A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

STOCK STANDARD SOLUTIONS - These solutions may be obtained as certified solutions or prepared from pure standard materials using the following procedures:

Prepare stock standard solutions (5000 µg/ml) by accurately weighing about 0.0500 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

PRIMARY DILUTION STANDARD SOLUTIONS - Use stock standard solutions to prepare primary dilution standard solutions that contain the analyte in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standard solutions also applies to primary dilution standard solutions.

III **SAMPLE COLLECTION, PRESERVATION AND STORAGE**

Sample Collection

Collect all samples in 40-mL bottles into which 3 mg of sodium thiosulfate crystals have been added to the empty bottles just prior to shipping to the sampling site. Alternately, 75 µl of freshly prepared sodium thiosulfate solution (0.04 g/mL) may be added to empty 40-mL bottles just prior to sample collection.

When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream.

When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill 40-mL sample bottles.

Sample Preservation

The samples must be chilled to 4°C at the time of collection and maintained at the temperature until the analyst is prepared for the extraction process. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to insure that they will be maintained at 4°C until arrival at the laboratory.

Sample Storage

Store samples and extracts at 4°C until extraction and analysis.

Extract all samples as soon as possible after collection. Results of holding time studies suggest that acetochlor is adequately stable for at least 14 days when stored under these conditions.

SUMMARY OF METHOD

Thirty-five mL of sample are extracted with 2 mL of hexane. Two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner in order to compensate for possible extraction losses.

The extraction and analysis time is 30 to 50 min per sample.

IV SAMPLE PREPARATION

Remove samples from storage and allow them to equilibrate to room temperature.

Remove the container caps. Withdraw and discard a 5-mL volume using a 10-mL graduated cylinder. Replace the container caps and weigh the containers with contents to the nearest 0.1 g and record these weights for subsequent sample volume determinations.

V EXTRACTION AND ANALYSIS

Remove the container cap of each sample, and add 6 g NaCl to the sample bottle. Using a transfer or automatic dispensing pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Invert the bottle and allow the water and hexane phases to separate.

Remove the cap and carefully transfer approximately 0.5 mL of hexane layer into an autosampler vial using a disposable glass pipet.

Transfer the remaining hexane phase, being careful not to include any of the after phase, into a second autosampler vial. Reserve this second vial at 4°C for an immediate reanalysis if necessary.

Transfer the first sample vial to an autosampler set up to inject 1-2 µL portions into the gas chromatograph for analysis. Alternately, 1-2 mL portions of samples, blanks, and standards may be manually injected, although an automsampler is strongly recommended.

Determination of Sample Volume in Bottles Not Calibrated

Discard the remaining sample/hexane mixture from the sample bottle. Shake off the remaining few drops using short, brisk wrist movements.

Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight (in grams) is equivalent to the volume (in mL) of water extracted. By alternately using 40-mL bottles precalibrated at 35-mL levels, the gravimetric steps can be omitted, thus increasing the speed and ease of this extraction process.

Calibration and Standardization

At least three calibration standards are needed; five are recommended. One should contain the analyte at a concentration near but greater then the method detection limit; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.02 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.04 µg/L, 0.10 µg/L, and 0.20 µg/L.

To prepare a calibration standard (CAL), add an appropriate volume of a secondary dilution standard to a 25-mL aliquot of reagent water in a 40-mL bottle. Do not add less than 20 µl of an alcoholic standard to the reagent water. Use a 25-µL micro syringe and rapidly inject the alcoholic standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Mix by inverting and shaking the capped bottle several times. Aqueous standards must be prepared fresh daily.

Starting with the standard of lowest concentration, prepare, extract, and analyze each calibration standard and tabulate peak height or area response versus the concentration in the standard. The results are to be used to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. Alternatively, if the ratio of concentration to response (calibration factor) is a constant over the working range (20% RSD or less), linearity to the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for an analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard.

Single point calibration is an acceptable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close (±20% or less) to that of the unknowns. Do not use less than 20 µL of the secondary dilution standard solution to produce a single point calibration standard in a reagent water.

VI CALCULATIONS

Use the single point calibration or use the calibration curve or calibration factor to directly calculate the uncorrected concentration (Ci) of each analyte in the sample (e.g., calibration factor x response).

Calculate the sample volume (Vs) as equal to the net sample weight:

Vs = gross weight - bottle tare.

Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = \frac{35(Ci)}{(V_s)}$$

Results should be reported with an appropriate number of significant figures. Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and significant figure for lower concentrations.

VII CONFIRMATORY ANALYSIS

All acetochlor identifications should be confirmed by using at least one additional qualitative technique. Positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, eg., mass spectrometry, Nitrogen/Phosphorus selective detector, or the use of a second chromatography column. Suggested alternative columns are included in EPA method 505 (Reference 1).