Lasso (Alachlor)

Method number:	PV2035
Target concentration:	0.5 mg/m^3 There is no OSHA PEL for Lasso. Neither NIOSH nor ACGIH has a recommended standard for Lasso. For the purpose of this study, the target concentration has been arbitrarily set at 0.5 mg/m^3. It represents 100x the detection limit for the proposed method.
Procedure:	Collection on a glass fiber filter (GFF) with backup pad (BUP), extraction of both the GFF and BUP separately with acetonitrile, and analysis by high performance liquid chromatography (HPLC) at two wavelengths, 214 nm, and 254 nm.
Recommended air Volume and sampling rate:	100 minutes at 1 Lpm (100 L)
Detection limit:	0.005 mg/m^3 (overall procedure based on the recommended air volume)
Status of method:	Partially Validated method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

Recently the OSHA Analytical Laboratory received a set of field samples requesting analysis for Lasso. The air samples had been collected on glass fiber filters. This report describes the analytical procedure developed and the preliminary validations of the sampling method. Lasso (Alachlor) is a pre-emergence herbicide. There have been several schemes proposed for the quantitative analysis of Lasso. Most of these involved the use of gas chromatography analysis of soil, crops, and water. (Ref. 5.1) Judging from its physical properties, glass fiber filters with backup pads may be a suitable collection medium for air samples of Lasso.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy)

Possible genetic damage by the herbicide, Lasso was indicated by a paper. (Ref. 5.2)

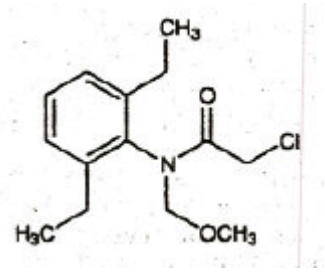
1.1.3 Potential workplace exposure

Lasso (Alachlor) is used in the pre-emergence controlling of broad-leaf weeds and grasses in soybeans, corn, and peanuts. Farmers used more than 20 million pounds in 1971. (Ref. 5.3)

1.1.4 Physical properties

CAS#	15972-60-8
Synonyms	Acetamide, 2-Chloro-N-(2-6 Diethylphenyl)-N-(Methoxymethyl) (9C); Alachlor; Alamex; Alochlor; 2-Chloro-2',6'-Diethyl-N-(methoxy methyl)acetamide; 2-Chloro-N (2,6-Diethyl)phenyl-N-Methoxymethylacetamide; CP 50144; Lasso; Lazo; Metachlor
Appearance:	Cream-colored solid
Molecular weight:	269.8
Melting point:	39.5 - 41.5 °C
Vapor pressure:	0.02 mmHg (100 °C)
Solubility:	soluble in ether, acetone, benzene, ethanol, and ethyl acetate
Molecular formula:	C_{14}-H_{20}-Cl-N-O_2

Structure:



1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 1.5 ng Lasso per injection. This is the amount of analyte which will give a peak whose height is approximately five times the amplitude of the baseline noise. See figure 1.

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is estimated to be 0.5 ug per sample or 0.005 mg/m^3 based on the recommended air volume, assuming 100% recovery from the sampling device. The recovery test at this level has not been performed.

1.2.3 Sensitivity

The sensitivity of the analytical procedure over a concentration range of 0.98 to 12.2 ug/mL is 47,890 area units per ug/mL of Lasso. The sensitivity is determined by the slope of the calibration curve. (See figure 2.)

1.3 Advantages

The analytical procedure is rapid, sensitive, and reproducible.

1.4 Disadvantages

1.4.1 The method has not been fully validated.

1.4.2 Both the glass fiber filter and the backup pad must be analyzed for Lasso separately.

2 Sampling Procedure

2.1 Apparatus

2.1.1 An air-sampling pump with a flow rate which can be calibrated to within ±5% of the recommended 1 Lpm flow rate while the sampler is in line.

2.1.2 Glass fiber filter, 37-mm diameter, Gelman Type A, or equivalent.

2.1.3 Backup pad, 37-mm diameter, Millipore AP100370, or equivalent.

2.1.4 Filter holder for 37-mm filters, Millipore M000037A0, or equivalent.

2.2 Sampling technique

2.2.1 Assemble the filter in the two-piece cassette holder and close firmly. The filter is supported by a backup pad. Secure the cassette holder together with tape.

2.2.2 Attach the outlet of the filter cassette to the personal sampling pump inlet with flexible tubing.

2.2.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

2.2.4 A sample size of 100 liters is recommended. Sample air at a flow rate of 1.0 liter/minute. The flow rate should be known with an accuracy of ±5%.

2.2.5 With each batch of samples, submit a blank filter from the same lot of filters used for the sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as a blank.

2.2.6 After sampling, seal cassette with a Form OSHA-21 seal.

2.2.7 The cassette should be shipped in a suitable container designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

2.2.8 A sample of the bulk material should be submitted to the laboratory in a glass container with a Polyseal cap. Never transport, mail, or ship the bulk sample in the same container as the sample or blank filter.

2.3 Retention efficiency

Three glass fiber filters were spiked with 49 ug of Lasso. 100 liters of humid air (85% relative humidity) was drawn through the filters at 1 Lpm. The recovery of the filter plus the backup pad was 93%.

Table 2.3
Retention Efficiency

sample #	µg spiked	peak area counts	% recovery
GFF-1	49	325,205	
BUP-1	none	78,049	91
GFF-2	49	377,738	
BUP-2	none	41,098	94
GFF-3	49	326,168	
BUP-3	none	88,949	94
Lasso std.	49	444,156	---
Lasso std.	49	442,351	---

2.4 Extraction efficiency glass fiber filter

The average extraction efficiency from the glass fiber fibers spiked with 49 ug of Lasso was 91%.

Table 2.4
GFF Extraction Efficiency

sample #	µg spiked	peak area counts	% recovery
1	49	404492	91
2	49	404168	91
3	49	410590	92
Lasso std.	49	444791	--
Lasso std.	49	444156	--

2.5 Extraction efficiency backup pad (BUP)

The average extraction efficiency from the backup pad spiked with 49 ug of Lasso was 102%.

Table 2.5
BUP Extraction Efficiency

sample #	µg spiked	peak area counts	% recovery
1	49	370752	103
2	49	370445	103
3	49	364837	103
Lasso std.	49	360045	---
Lasso std.	49	362759	---

2.6 Storage

Storage test was not done.

2.7 Recommended Air Volume and Sampling Rate

2.7.1 The recommended air volume is 100 liters.

2.7.2 The recommended sampling rate is 1 Lpm.

2.8 Interferences

There are no known interferences associated with the sampling procedure.

2.9 Safety Precautions

2.9.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical Method

3.1 Apparatus

3.1.1 High performance liquid chromatograph equipped with pump, sample injector, extended wavelength module, dual wavelength detector, chart recorder, and other necessary hardware.

3.1.2 HPLC reverse phase C-18 analytical column (DuPont Zorbax ODS) was used for this study.

3.1.3 An electronic integrator or other suitable method to measure detector response.

3.1.4 Microliter syringe or automatic sampling device for making sample injections.

3.1.5 Volumetric flasks of convenient sizes for preparing standards.

3.1.6 Shaking device for extraction of samples.

3.2 Reagents

3.2.1 Lasso (EPA standard 8452)
3.2.2 Acetonitrile, HPLC grade

3.2.3 Water, HPLC grade

3.3 Sample Preparation

3.3.1 Remove the filter from the cassette with clean tweezers and place it in a 20-mL scintillation vial.

3.3.2 Add 5 mL acetonitrile to the vial and cap it.

3.3.3 Shake the vials vigorously on a shaker for 30 minutes.

3.4 Standard Preparation

3.4.1 Standards of Lasso are prepared by dissolving 9 to 12 mg (accurately weighed) of Lasso in acetonitrile in a 10 mL volumetric flask and diluting to volume.

3.4.2 Dilute working range standards of 0.9 to 12 ug/mL with acetonitrile.

3.4.3 Store standards in dark bottles under refrigeration.

3.5 Analysis

3.5.1 HPLC Conditions

Column:	Zorbax ODS (25-cm x 4.6-mm)
Mobile Phase:	60% acetonitrile/40% water
Flow Rate:	1.1 mL/minute
Dual Wavelength Detector:	214 nm, 254 nm
Injection Volume:	15 uL
Retention Time:	12.4 minutes

3.5.2 Chromatogram

See Figure 1.

3.5.3 Peak magnitude is measured by electronic integrator or other means.

3.5.4 An external standard procedure is used to prepare a calibration curve from the analysis of at least three different concentrations from two separate weightings.

3.5.5 Bracket the sample with analytical standards.

3.6 Interferences (analytical)

3.6.1 Any collected compound that has the same LC retention time as analyte and absorbs at 214 nm and 254 nm is interference.

3.6.2 HPLC parameters may be varied to circumvent most interference.

3.6.3 Retention time alone is not proof of a chemical identity. Confirmation by other means should be sought when possible.

3.7 Calculations

3.7.1 The integrator value in area units for each standard is plotted against its concentration in ug/mL and a calibration curve using the best-fit straight line through the points is obtained.

3.7.2 Sample concentration is calculated from the calibration curve.

3.7.3 The air concentration of Lasso for a sample is calculated by the following equation:

$$mg / m^3 = \frac{(\mu g / mL,\ in\ sample)(extraction\ volume,\ mL)}{(air\ volume,\ L)}$$

3.8 Safety Precautions

3.8.1 Confine the use of solvents to a fume hood.

3.8.2 Wear safety glasses in all laboratory areas.

4 Recommendations for Further Study

4.1 Storage test

4.1.1 A complete storage test needs to be done.

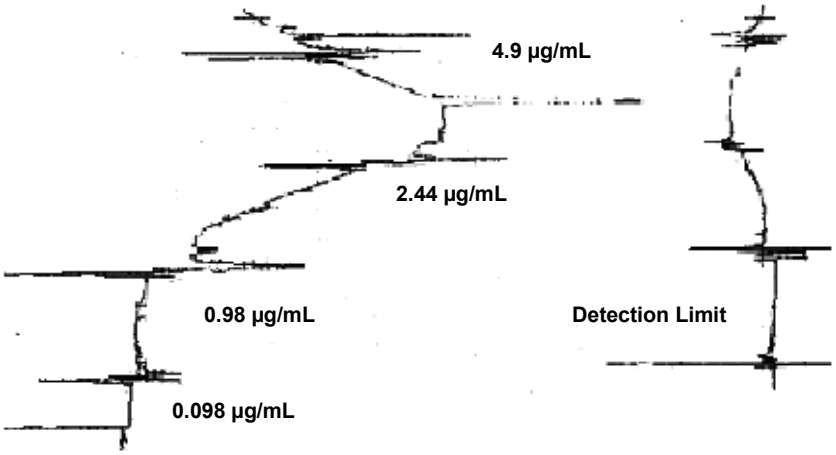


FIGURE 1. Lasso Detection Limit

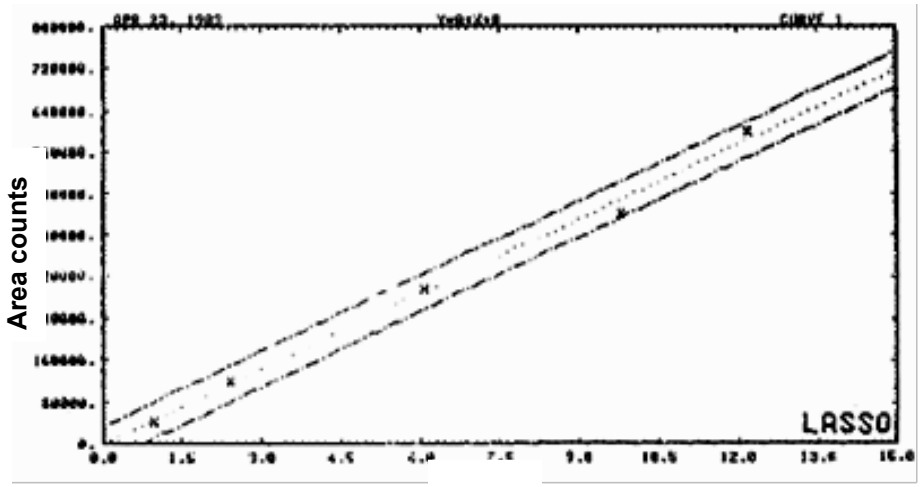


Figure 2. Calibration Curve

5 References

5.1 Amann, B.D.; Call, D.J.; Draayer, H.H.; J. Assoc. Off. Anal. Chem. 59(4), pp. 859-861, 1976.

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