

DETERMINATION OF PHENOXYCARBOXYLIC ACID HERBICIDES IN WATER

INTRODUCTION

The method allows determination of mass concentrations of herbicides classified as phenoxy-carboxylic acids, specifically: 2,4-dichlorophenoxybutyric acid (2,4-DB), 2,4-dichlorophenoxypropionic acid (2,4-DP, Dichlorprop), 2,4-dichlorophenoxyacetic acid (2,4-D), and phenoxyacetic acid in samples of natural, potable and treated waste water by capillary electrophoresis.

MEASURING METHOD

The capillary electrophoresis method for evaluation of 2,4-D class herbicides mass concentration is based on the migration and separation of these substances in the electric field due to their different electrophoretic mobility. Identification and quantitative evaluation of the analyzed components are performed by detecting the inherent UV absorption at a wavelength of 205 nm.

CONCENTRATION RANGES

Ranges of measurable concentrations for analyzed herbicides are given in Table 1.

Table 1. Measurement ranges for herbicides

Herbicide	Samples	Measurement range, mg/l
Phenoxyacetic acid	Potable, natural and waste water	0.2–20
2,4-D	Potable, natural and waste water	0.2–20
2,4-DP	Potable, natural and waste water	0.2–20
2,4-DB	Potable, natural and waste water	0.2–20

If minimal concentrations should be detected (less than 0.2 mg/l), the sample must be concentrated by solid-phase extraction, in this case the range of detectable concentrations will be 0.002–0.2 mg/l for a 100-ml sample.

Humic acids, if below 50 mg/l, do not hinder determination of subject components.

Analyzed herbicides decompose in aqueous media to form 2,4-dichlorophenol, which completely separates with subject components during analysis and does not prevent their proper determination.

EQUIPMENT AND REAGENTS

The following equipment and reagents are used in measurements:

- The CAPEL-105 Capillary Electrophoresis System with high-voltage positive polarity;
- Reference PAA, 2,4-DPAA, 2,4-DPPA and 2,4-DPBA content standard solutions with a mass concentration of 1 mg/l;
- DIAPAK C16 concentrating cartridges;
- Distilled water;
- Anhydrous sodium sulfate, Ultra Pure Grade;
- Acetone, Analytical Grade;
- Acetonitrile, High Purity Grade;
- Sodium hydroxide, Ultra Pure Grade;
- Hydrochloric acid, Ultra Pure Grade.

Data acquisition, collection, processing and output are performed using a personal computer running under WINDOWS® 95/98/ME/NT/2000 operating system with installed Chrom&Spec® for WINDOWS® software package for acquisition and processing of chromatography data.

PREOPERATIONAL PROCEDURES

Preoperational procedures include: selection and preparation of samples, preparation of the capillary to operation, preparation of auxiliary and calibration solutions, and calibration of the CAPEL Capillary Electrophoresis System.

Samples of natural, potable or waste water should be collected in compliance with ISO 5667 Standard. Volume of the sample should be at least 100 ml for direct

analysis and no less than 500 ml if concentrating the sample is necessary. The sample taken (no less than 50 ml) should be filtered through a cellulose-acetate filter; first portion of the filtrate must be discarded. The sample must be analyzed within 24 hours.

The system is calibrated by measuring signals of calibration solutions.

Stability of the calibration characteristics is checked directly before sample measurement by recording an electropherogram of one of the calibration mixtures.

MEASUREMENT PROCEDURE

No less than two specimens should be analyzed for each sample queued. If the measured concentrations of herbicides exceed the upper limit of calibration curve, it is necessary to pre-dilute the sample with distilled water. If low concentrations of herbicides are measured (below 0.2 mg/l), the sample should be concentrated with DIAPAK C16 concentrating cartridges.

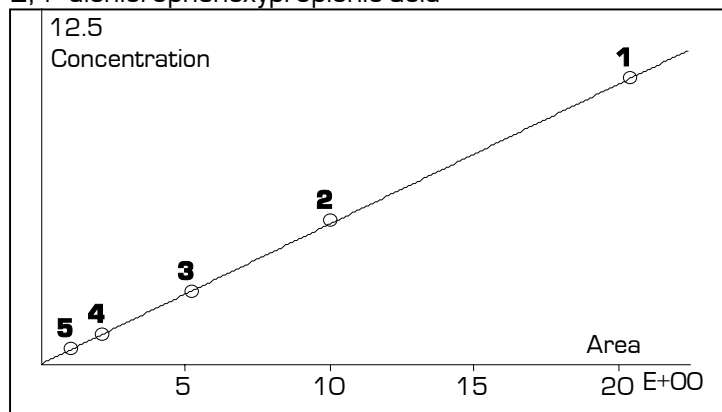
DATA PROCESSING

Chrom&Spec® for WINDOWS® software outputs a report of mass concentrations (in mg/l) of analyzed herbicides in the solution prepared for analysis.

EXAMPLE OF REAL ANALYSIS

Calibration curve:

2,4-dichlorophenoxypropionic acid



Component	Equation	RSD, %	Correlation, r
Phenoxyacetic acid	$Q=1.1732A$	1.17	0.999
2,4-D	$Q=0.5545A$	2.04	0.999
2,4-DP	$Q=0.4907A$	1.49	0.999
2,4-DB	$Q=0.8007A$	1.39	0.999

Sample test solution, ca. 2.5 mg/l of each compound
Buffer 10 mmol sodium borate
Capillary L_{EFF}/L_{TOTAL} 60/70 cm, id 75 μ m
Injection 900 mbar*s
Voltage +20 kV
Detection 205 nm

- 1** – 2,4-dichlorophenoxybutyric acid
- 2** – 2,4-dichlorophenoxypropionic acid
- 3** – 2,4,5-trichlorophenoxyacetic acid
- 4** – 2,4-dichlorophenoxyacetic acid
- 5** – 2,4-dichlorophenol
- 6** – phenoxyacetic acid

