

## Determination of 2,4-D in aqueous solution by neutron activation analysis

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A method based on neutron activation analysis was developed for the determination of fractions of milligrams of 2,4-D (2,4-dichlorophenoxy acetic acid) in aqueous solution in laboratory tests. The indirect determination of 2,4-D was based on the quantification of chlorine, <sup>38</sup>Cl, produced by neutron activation. The range of application was 0.01–100 mg l<sup>-1</sup>. No loss of <sup>38</sup>Cl by chemical effects of the nuclear reaction was found. The advantages of the proposed method include high precision and sensitivity of determination. Results were compared with those obtained by UV-Vis spectrophotometry, where concentrations less than 1 mg l<sup>-1</sup> were not detected.

### Introduction

Chlorophenoxy acids, such as 2,4-dichlorophenoxy acetic acid (2,4-D, C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>OCH<sub>2</sub>COOH) formulated as salts or esters are still widely used for the control of weeds in dams, hay and pasture crops, cereal fields and also as growth regulators of citrus fruits.<sup>1</sup> Although their persistence in soils is about 1 to 5 months, higher persistence is to be expected in water with lower biological activity.<sup>2</sup> The high solubility of phenoxy acids in water promotes their entry into surface- or ground-water.<sup>3,4</sup>

The continued application of phenoxy acid herbicides and growing concerns about the potential contamination of water require regulations, such as the Mexican Drinking Water Ordinance, which set an upper limit for 2,4-D concentrations of 50 µg l<sup>-1</sup>.<sup>5</sup> The detection limits for drinking water proposed as health advisory level for 2,4-D have been established by the Office of Water of the US Environmental Protection Agency as 70 µg l<sup>-1</sup>. Its toxicity to humans and organisms demands the development of sensitive and selective analysis methods.<sup>6</sup>

Traditional analytical methods used in herbicide analysis are generally time-consuming. Standard methods for the determination of herbicides by gas chromatography (GC) involve liquid-liquid extraction of the sample and concentration and derivatization, with or without additional cleanup.<sup>7,8</sup> Recently, these methods have been successfully replaced by solid-phase extraction in off-line or on-line modes, followed by high pressure liquid chromatography (HPLC) with ultraviolet (UV) or mass spectrophotometric (MS) detection.<sup>9,10</sup>

Alternative procedures are proposed by EREMIN et al.<sup>11</sup> with photochemical fluorimetric detection. The main advantages of this method are its rapidity and the low cost of the required equipment, but it is

influenced by the organic solvent, pH, methanol percentage and the UV irradiation time on the excitation and emission wavelengths and fluorescence intensity.

Chlorophenoxy acid herbicides can be analyzed by capillary and electrophoresis methods,<sup>12</sup> which have the following advantages: high resolution, high separation efficiency but have no good reproducibility.

UV-Vis spectrophotometry has been used for 2,4-D determination,<sup>4,13</sup> this is a fast method but only applicable to concentrations higher than 3 mg l<sup>-1</sup>.

Since the purpose of the present study was to develop a fast, reliable method for the determination of 2,4-D in aqueous solutions for laboratory tests, neutron activation analysis (NAA) and UV-Vis spectrophotometry were those chosen for testing. Aspects of the effects of (n,γ) reactions were investigated. This paper is part of a general study which evaluates the retention capacity of clays and zeolites for organic contaminants present in waters in Mexico.

### Experimental

Neutron activation and UV-Vis spectrophotometry analysis were tested and calibrated with a high purity 2,4-D standard (99.9%), (Chem. Service, USA). The methods were applied to a commercial solution called hierbamine (CIBA-GEIGY, Mexico), used in the crop areas of Central Mexico, which contains 2,4-D dimethylamine salt (49% of 2,4-D). Working solutions from 0.01 to 100 mg l<sup>-1</sup> were prepared by the suitable dilution of standard and hierbamine solutions.

#### Neutron activation analysis

The indirect determination of 2,4-D was based on the quantification of <sup>38</sup>Cl. 1 ml of hierbamine, and standard solutions, having been sealed in small polyethylene

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capsules, were inserted in the standard polyethylene irradiation containers.  $^{38}\text{Cl}$  was obtained by neutron irradiation of 2,4-D for 15 to 35 minutes in a Triga Mark III reactor with a neutron flux of  $10^{12}$ – $10^{13}$   $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ . The irradiation was carried out in a fixed irradiation system. Immediately upon removal from the reactor, the samples were taken to the radiochemistry laboratory where the containers were opened and the samples analyzed.  $^{38}\text{Cl}$  was determined by  $\gamma$ -spectrometry. Gamma radiation was measured with a Ge/hyperpure solid-state detector coupled to a 4096 channel pulse-height analyzer. All spectra were stored on disks of a personal computer. The NUCLEOS program was utilized to calculate the energy and peak area at 1642 Kev for  $^{38}\text{Cl}$  produced by the  $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$  nuclear reaction. The  $\gamma$ -ray spectra of 2,4-D standard and hierbamine showed no interference from other isotopes.

Loss of  $^{38}\text{Cl}$  by effects of the  $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$  nuclear reaction was evaluated in the following way. Quartz vials were filled with the 2,4-D standard and hierbamine solutions and were sealed at vacuum. After neutron irradiation,  $^{38}\text{Cl}$  was measured before and after the vials were opened.

#### UV-Vis spectrophotometric analysis

UV-Vis spectrophotometric measurements were performed at 283  $\text{nm}^4$  by using a Magna-IR 550 UV-Visible spectrophotometer. A calibration curve was drawn before each analysis. The average values were based on three replicate analyses.

## Results and discussion

Since (n,  $\gamma$ ) reactions generally produce, chemical changes of the compounds containing the element being activated, we wanted to determine whether the  $^{37}\text{Cl}$  (n,  $\gamma$ ) $^{38}\text{Cl}$  reaction produced volatile  $^{38}\text{Cl}$  compounds which could be lost during the process. We did not find any loss of  $^{38}\text{Cl}$ . The  $^{38}\text{Cl}$  compounds produced by the nuclear reaction were soluble in the solution; therefore, it was possible to utilize the presence of  $^{38}\text{Cl}$  as an indirect measure of 2,4-D. By NAA, 6 samples can be analyzed in 1.5 hours.

In order to evaluate the analytical usefulness of the neutron activation method, analyses of 2,4-D were carried out on the standard samples, using  $\gamma$  spectrometry. Analytical results are shown in Table 1. It can be observed that satisfactory results were obtained with coefficients of variation from 1.0 to 5.7%. The values show a high precision in measurements of the standard solution in the range from 0.01 to 100  $\text{mg}\cdot\text{l}^{-1}$ .

Table 1 also shows the results obtained by UV-Vis spectrophotometric analyses of the 2,4-D standard solution. Its determination was possible only for concentrations higher than 1  $\text{mg}\cdot\text{l}^{-1}$ . The coefficients of variation were lower for concentrations higher than 3  $\text{mg}\cdot\text{l}^{-1}$ ; however, for lower concentrations the coefficients increased up to 60%. In this case, high precision for concentrations between 5 to 100  $\text{mg}\cdot\text{l}^{-1}$  was found.

Table 1. Neutron activation and UV-Visible spectrophotometric analyses of 2,4-D standard solutions

Concentration, $\text{mg}\cdot\text{l}^{-1}$	Neutron activation analysis		UV-Vis spectrophotometric	
	Concentration, $\text{mg}\cdot\text{l}^{-1}$	Coefficient of variation, %	Concentration, $\text{mg}\cdot\text{l}^{-1}$	Coefficient of variation, %
100	100 $\pm$ 4.942	4.9	100 $\pm$ 1.98	2.0
75	75 $\pm$ 2.141	2.8	75 $\pm$ 0.54	0.7
50	50 $\pm$ 1.754	3.5	52 $\pm$ 0.26	0.5
25	25 $\pm$ 0.813	3.3	25 $\pm$ 0.33	1.3
10	10 $\pm$ 0.280	2.9	10 $\pm$ 0.18	1.8
7.5	7.5 $\pm$ 0.074	1.0	7.0 $\pm$ 0.30	4.3
5.0	5.0 $\pm$ 0.060	1.2	5.0 $\pm$ 0.27	5.6
2.5	2.5 $\pm$ 0.030	1.2	3.0 $\pm$ 0.66	21.6
2.0	2.0 $\pm$ 0.033	1.7	1.0 $\pm$ 0.60	43.2
1.0	1.0 $\pm$ 0.022	2.0	0.9 $\pm$ 0.52	60.5
0.9	0.9 $\pm$ 0.024	2.7	ND	
0.8	0.8 $\pm$ 0.018	2.3	ND	
0.7	0.7 $\pm$ 0.018	2.6	ND	
0.6	0.6 $\pm$ 0.019	3.1	ND	
0.5	0.5 $\pm$ 0.021	4.2	ND	
0.4	0.4 $\pm$ 0.016	4.0	ND	
0.3	0.3 $\pm$ 0.013	4.3	ND	
0.2	0.2 $\pm$ 0.003	4.2	ND	
0.1	0.1 $\pm$ 0.004	4.1	ND	
0.05	0.05 $\pm$ 0.001	2.1	ND	
0.025	0.025 $\pm$ 0.001	4.5	ND	
0.01	0.01 $\pm$ 0.001	5.7	ND	

ND – Not determined.

Table 2. Neutron activation and UV-Vis spectrophotometric analyses of hierbamine solutions

NAA		UV-Vis spectrophotometric	
Concentration, mg·l <sup>-1</sup>	Coefficient of variation, %	Concentration, mg·l <sup>-1</sup>	Coefficient of variation, %
97.4 ± 2.771	2.94	101.7 ± 0.18	0.17
72.1 ± 1.382	1.87	77.3 ± 0.16	0.21
49.6 ± 1.412	2.83	51.4 ± 0.08	0.16
26.8 ± 1.301	4.94	25.4 ± 0.07	0.27
11.9 ± 0.790	6.79	10.1 ± 0.17	1.68
10.8 ± 0.290	3.02	9.4 ± 0.16	1.78
5.6 ± 0.100	1.84	5.5 ± 0.30	5.41
3.1 ± 0.311	3.68	3.4 ± 0.25	7.21
2.3 ± 0.201	3.64	2.4 ± 0.29	12.66
0.9 ± 0.031	3.74	0.3 ± 0.27	91.16
1.1 ± 0.009	2.72	ND	
0.78 ± 0.020	3.58	ND	
0.72 ± 0.022	4.58	ND	
0.69 ± 0.051	6.81	ND	
0.51 ± 0.009	2.32	ND	
0.39 ± 0.020	4.16	ND	
0.28 ± 0.033	11.65	ND	
0.059 ± 0.019	3.30	ND	
0.038 ± 0.004	1.11	ND	
0.0102 ± 0.005	5.03	ND	

ND – Not determined.

Table 2 shows the analyses of 2,4-D in hierbamine by both techniques. The measurement of 2,4-D in the hierbamine by NAA showed a higher fluctuation of the coefficients of variation, from 1.1 to 6.8%; however, these values are quite acceptable, and for concentrations lower than 9 mg·l<sup>-1</sup> the coefficients of variation are much lower than the corresponding values determined by UV-Vis spectrophotometry (5.4 to 91.2%). It was also found that for concentrations higher than 9 mg·l<sup>-1</sup> UV-Vis spectrophotometric analysis was more precise than NAA.

Our results for UV-Vis spectrophotometric analysis are similar to those of QUE HEE and SUTHERLAND,<sup>13</sup> who reported an application range from 6 to 250 mg·l<sup>-1</sup> and by CLARKSON et al.,<sup>4</sup> who measured concentrations between 3 and 250 mg·l<sup>-1</sup>.

### Conclusions

2,4-D is an important herbicide in environmental chemistry on account of its toxicity. Using the methods developed in this paper, one may correctly measure 2,4-D concentration by NAA by observing the activity of <sup>38</sup>Cl. The method is attractive because of its simplicity compared with tedious chemical processes; moreover, it is precise with a coefficient of variation of 1.1 to 6.8%, for concentrations of hierbamine ranging from 0.01 to 100 mg·l<sup>-1</sup>. However, for concentrations higher than 5–10 mg·l<sup>-1</sup>, UV-Vis spectrophotometric analysis is a better means of detecting 2,4-D in hierbamine because of better precision and readily available equipment. For lower concentrations (5 mg·l<sup>-1</sup>), the precision is too low

and for concentrations less than 1 mg·l<sup>-1</sup> there is no response.

We can conclude that nuclear activation analysis is a simple, precise and quite sensitive method for the determination of 2,4-D herbicide in laboratory tests.

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