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Fast screening method for eight phenoxyacid herbicides and bentazone in water

Optimization procedures for flow-injection analysis–thermospray tandem mass spectrometry

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ABSTRACT

The development of a screening method for the rapid screening of water samples for phenoxyacid herbicides and bentazone with flow-injection analysis–thermospray tandem mass spectrometry is described. A two-step optimization procedure was used to determine the optimum instrumental parameters. First, introducing the analytes of interest continuously, the vaporizer temperature, discharge voltage and repeller voltage were changed stepwise over a wide range under computer control. With different solvent mixtures and source block temperatures, the carrier stream with which the highest molecular (parent) ion intensities were obtained in the single scan Q3-MS scan mode was selected. This turned out to be 0.1 *M* aqueous ammonium acetate–acetonitrile (90:10, v/v). For phenoxyacid herbicides and bentazone negative ionization with buffer-assisted ion evaporation (ammonium acetate) gave the most intense parent ions. The discharge voltage had little influence on the signal intensities and a low repeller voltage turned out to be the best for all analytes. Next, the optimum collision gas pressure and collision offset voltage were determined. The most intense daughter ions were derived with a collision gas pressure (argon) of 3–4 mTorr (1 Torr = 133.322 Pa) and a collision offset voltage of 18 eV for phenoxyacid herbicides and 22 eV for bentazone. In order to obtain maximum sensitivity, a multiple reaction monitoring method was used in which two parent ion–daughter ion pairs were monitored for each phenoxyacid herbicide and one parent ion and three daughter ions for bentazone. Without sample concentration all eight phenoxyacid herbicides and bentazone can be determined at the low μg/l level. The method is fully automated; with a 5-ml loop injection and the subsequent cleaning runs the analysis time is 10 min. The detection limit is *ca.* 1 μg/l with linear calibration graphs up to 50 μg/l. The method was used to confirm the presence of bentazone and the absence of the phenoxyacid herbicides in a surface water sample.

INTRODUCTION

Phenoxyacid herbicides and bentazone are widely used in agriculture. They are toxic and environmentally persistent for several months. These compounds are readily soluble in water and their runoff from cropland into rivers and lakes is considerable. Allowable concentration levels in Dutch inland waters depend on the type of compound and are between 0.1 and 11 μg/l for phenoxyacid herbicides [1]. As surface water is used for the production of drinking water there is a need for continuous monitoring. The

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European Community (EC) has set the maximum allowable concentration for individual pesticides at 0.1 μg/l for drinking water [2]. In our institute (RIZA), the chlorophenoxy carboxylic acid herbicides 4-chloro-2-methylphenoxyacetic acid (MCPA), (2,4-dichlorophenoxy)acetic acid (2,4-D), 2-(4-chloro-2-methylphenoxy)propionic acid (MCPP), 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP), (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB), 4-(4-chloro-2-methylphenoxy)-butyric acid (MCPB) and (2,4,5-trichlorophenoxy)propionic acid (2,4,5-TP) and bentazone are determined in surface and waste waters with a previously described fully automated liquid chromatographic (LC) method with UV detection [3,4].

With mass spectrometric (MS) detection, phenoxyacid herbicides can be determined with direct liquid introduction [5], particle beam [6,7] or with a thermospray interface in the negative-ion mode using filament-off, filament-on or discharge ionization modes [8–13]. In an attempt to provide additional structural information, chloroacetonitrile is added to the eluent [8,12,14].

The use of tandem mass spectrometry (MS–MS) permits rapid analyses for specific compounds [15]. The sensitivity levels obtained are generally *ca.* 100 pg [16] without the need for the chromatographic separation [17–19]. Although environmentally important compounds have been studied [13,16–24], few data on the (LC)–MS–MS of pesticides or polar hydrophilic compounds in aqueous samples have been published.

To achieve the lowest possible detection limits for a targeted compound with (LC)–MS–MS, single reaction monitoring (SRM) should be performed [25]. If a larger number of compounds need to be determined, the MS–MS conditions must be of "general" adjustment or they must be continuously changed to obtain optimum results for each compound.

In this study, it was our aim to develop a rapid screening method, preferably at the 0.1 μg/l level, for phenoxyacid herbicides and bentazone in aqueous samples. Optimization procedures for flow-injection analysis–thermospray tandem mass spectrometry (FIA–TSP-MS–MS) were written for a Finnigan TSQ-70 instrument including a TSP-2 interface. Most of the parameters were adjusted by the software and, except for the collision gas and the source block temperature, parameters such as the collision offset voltage, repeller voltage, discharge voltage and vaporizer temperature could be instantaneously (μs–s) changed by the data system.

EXPERIMENTAL

Reagents

Water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). HPLC-grade acetonitrile, formic acid, trifluoroacetic acid (used as tuning solvent) and ammonium acetate were obtained from J.T. Baker (Deventer, Netherlands). Ammonium formate was obtained from Sigma (St. Louis, MO, USA). All chlorophenoxy carboxylic acids were obtained from Riedel-de Haën (Hannover, Germany) and bentazone from Promochem (Wesel, Germany).

Apparatus

An LKB (Bromma, Sweden) Model 2150 pump was used to deliver the FIA carrier stream at a flow-rate of 1.5 ml/min.

For Procedures I and II (see below) the analytes were dissolved in the appropriate solvent mixture at concentrations of 500 or 50 μg/l and continuously introduced into the MS–MS system.

An ASPEC (Gilson, Villiers-le-Bel, France) was used to inject samples with a 3- or 5-ml loop into the carrier stream. After each injection, an injection with pure water and an injection with acetonitrile were made to ensure complete cleaning of the total system including the thermospray interface. Also, the optimum repeller voltage in the single MS scan mode (Q3-MS) with regard to the intensity and mass assignment of the parent ions was checked daily by injecting a 50 μg/l standard solution in 0.1 *M* aqueous ammonium acetate–acetonitrile (90:10, v/v).

A Finnigan TSQ-70 mass spectrometer (Finnigan Mat, San Jose, CA, USA) equipped with a Finnigan thermospray interface (TSP-2) was used. The conversion dynode was set at 15 kV, the electron multiplier at 1.5–2.0 kV and the electrometer amplifier gain at 10^{-8}. Argon was

used as the collision gas. All optimization procedures were written in Finnigan's instrument control language.

Sample handling

Stock solutions of the phenoxyacid herbicides and bentazone were prepared by dissolving *ca.* 25 mg of each compound in 50 ml of acetonitrile. From these solutions a mixed standard solution was prepared and diluted with Milli-Q-purified water, 0.1 *M* ammonium acetate, 0.1 *M* ammonium formate or 0.1 *M* formic acid (in Milli-Q-purified water) to obtain a series of solutions that contained 10 vol.% of acetonitrile and 500, 50, 5, 1, 0.5, 0.25, 0.125 or 0.1 μg/l of each analyte.

Optimization procedures

Two stepwise optimization procedures were used to determine the optimum instrumental parameters. First (Procedure I, Fig. 1), introducing the analytes of interest continuously, the vaporizer temperature, discharge and repeller voltage were changed stepwise over a wide range under computer control with different solvent mixtures and source block temperatures in the single-scan Q3-MS scan mode.

From the data obtained, the conditions that gave the highest molecular ion $[M-1]^-$ intensities were selected and used in Procedure II. For the phenoxyacid herbicides the parent ion masses were *m/z* 199, 213, 219, 227, 233, 247, 253 and 267 and for bentazone *m/z* 239.

Second (Procedure II), the optimum collision offset voltage that gave the highest daughter ions was selected at different collision gas pressures for the selected molecular ions in the daughter-ion scan mode. For the monochloro phenoxyacid herbicides the daughter ion mass was *m/z*, 141, for the dichloro phenoxyacid herbicides *m/z* 161, for the trichloro phenoxyacid herbicides *m/z* 195 and for bentazone *m/z* 132, 133 and 197.

In Procedure I the vaporizer temperature is increased stepwise (5°C per step) from 75 to 130°C. At every adjustment the discharge voltage goes stepwise from 0 to 2000 V at 250 V per step and during every adjustment of the discharge voltage the repeller voltage goes stepwise from 0 to −200 V at 20 V per step. The scantime was 2 s and the scan range *m/z* 90–350. The complete cycle takes *ca.* 40 min and produces *ca.* 1100 data. Procedure I was carried out for source block temperatures of 100, 150, 200 and 250°C and for all solvent mixtures.

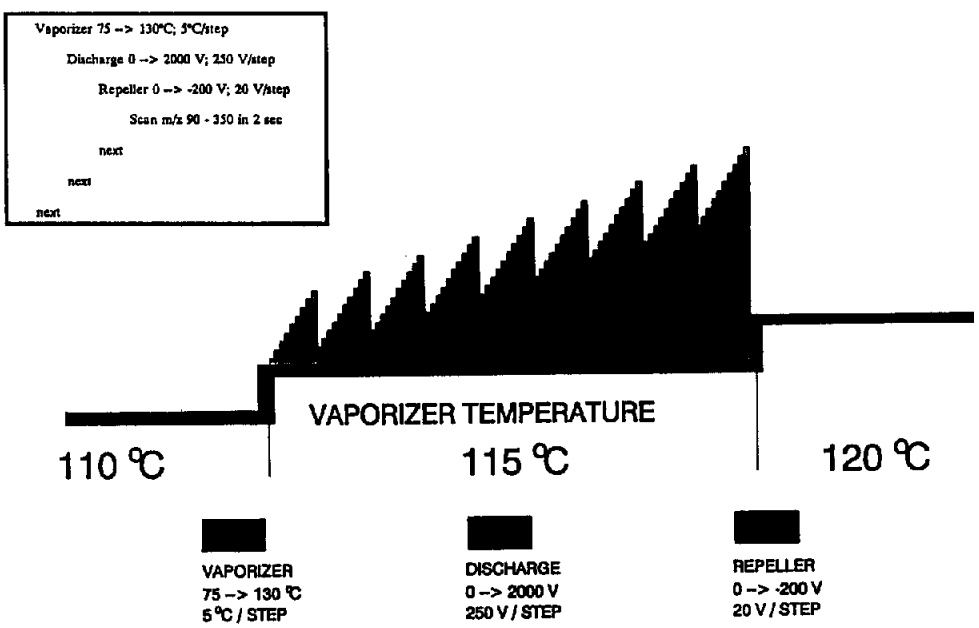

Fig. 1. Illustration of optimization Procedure I; for details, see Experimental.

In Procedure II the collision offset voltage is determined at different collision gas pressures to acquire daughter ion signals of the parent ions selected with Procedure I. In this procedure the collision offset voltage is increased stepwise at 2 eV per step from 0 to 50 eV, using collision gas (argon) pressures of 1, 2, 3, 4 and 5 mTorr (1 Torr = 133.322 Pa). From the data obtained the collision gas pressure, collision offset voltage and daughter ions are selected.

RESULTS AND DISCUSSION

With MS–MS, selected (single or multiple) reaction monitoring (SRM or MRM, respectively) is often used in trace analysis in which a limited number of parent ion–daughter ion pairs are monitored for each analyte to give maximum sensitivity [26]. MS–MS methods can be used to detect and confirm amounts of analytes as low as 100 pg [16,27]. In order to do so, it is desirable that the primary ionization conditions give an abundant high-mass ion preferably indicative of the molecular mass in the first mass analyser. Collisionally activated dissociation (CAD) with neutral gas molecules then produces characteristic fragments that can be identified in the second mass analyser. The yield of these so-called daughter ions determines the analytical sensitivity and therefore the detection limit of the MS–MS procedure. Unfortunately, optimum conditions for the operating parameters are different for every class of compound and, often, even for every individual analyte within a certain class.

The optimization procedures presented here were written to select optimum conditions in terms of sample solution, source block and vaporizer temperature, discharge and repeller voltage, collision offset voltage and collision gas pressure.

Sample solution, source and vaporizer temperature

The sample solutions used in the experiments were 90:10 (v/v) mixtures of water, 0.1 *M* formic acid, 0.1 *M* ammonium acetate or 0.1 *M* ammonium formate and acetonitrile.

In Table I the results are given that were obtained using Procedure I (see Experimental). The data in each column of Table I were obtained from one spectrum. A source block temperature of 200°C, a sample solution containing 0.1 *M* ammonium acetate and a vaporizer temperature of 105–110°C gave the most intense

TABLE I

INTENSITIES ($\times 10^6$) OF MOLECULAR IONS OF PHENOXYACID HERBICIDES AND BENTAZONE IN VARIOUS SAMPLE SOLUTIONS AT DIFFERENT SOURCE BLOCK TEMPERATURES USING OPTIMIZATION PROCEDURE I

The sample solutions used in the experiments were 90:10 (v/v) mixtures of water, 0.1 *M* formic acid, 0.1 *M* ammonium acetate or 0.1 *M* ammonium formate and acetonitrile. A source block temperature of 100°C gave unstable vaporizer temperatures and are not reported; a source block temperature of 250°C was not measured for all solvents.

Analyte	m/z[a]	Water			Formic acid		Ammonium acetate			Ammonium formate	
		150°C	200°C	250°C	150°C	200°C	150°C	200°C	250°C	150°C	200°C
MCPA	199	3.8	3.3	4.8	11.9	11.5	13.9	14.9	14.9	11.4	11.2
MCPP	213	4.5	6.3	6.1	11.9	9.4	12.8	14.0	13.3	11.6	11.2
2,4-D	219	9.2	1.3	2.7	9.2	6.4	6.9	9.5	9.0	7.1	5.8
MCPB	227	2.0	1.7	1.1	4.3	2.3	10.4	9.4	6.4	3.3	2.9
2,4-DP	233	8.2	2.8	4.7	8.2	8.6	9.6	11.5	7.4	7.0	6.1
Bentazone	239	0.82	0.65	0.58	2.0	1.6	14.6	13.4	12.3	13.1	10.7
2,4-DB	247	0.68	0.57	0.39	7.3	4.0	5.4	5.6	2.7	5.2	3.5
2,4,5-T	253	0.7	0.6	0.7	3.5	3.0	3.6	4.8	2.1	4.8	3.2
2,4,5-TP	267	1.5	1.6	1.6	8.3	5.6	8.7	9.5	5.7	9.5	7.4

[a] $m/z = [M - 1]^-$.

molecular ions for all compounds. Vaporizer temperatures higher than 115°C gave, with all solutions and at all source block temperatures, increased fragmentation of the molecular ion to low m/z fragments (see Fig. 2; scan 820–1100), while vaporizer temperatures below 100°C (Fig. 2; scan 0–460) gave less intense signals of the molecular ions. During optimization it turned out that a source block temperature of 100°C was too low to give stable vaporizer temperatures. The results obtained with a source block temperature of 250°C were similar to those at 200°C. Therefore, some sets of data obtained at the former temperatures have not been included in Table I.

Using Procedure I, for all four sample solutions and pure water, background signals of solvent adducts were recorded at a source block temperature of 200°C in order to detect whether any interfering peaks would show up. No such interferences with the parent scan masses were observed.

Solvent adducts with the molecular ion were absent with water as sample solvent but with the other solutions signals at $[M + CH_3COO]^-$ for ammonium acetate (relative abundance 5%) and $[M + HCOO]^-$ for formic acid (relative abundance 10–20%) and ammonium formate (relative abundance <50%) were observed. In the literature [8,10,12], these adducts are sometimes reported as the base peaks.

Discharge and repeller voltage

Fig. 3 shows an expansion of part of the data generated in Procedure I, *viz.*, for vaporizer temperatures of 105, 110 and partly 115°C. Low repeller voltages give intense signals whereas higher repeller voltages give only uniform effects. At 110°C the discharge voltage is much more irregular than at 105°C, while at 115°C the signals are strongly decreased, as explained above. Note the m/z 40 which is the vaporizer temperature and the starting point of a cycle at a new vaporizer temperature (see also legend Fig. 3). From this scan number the repeller voltage value and the discharge voltage value can be easily determined in the cycle, which has nine discharge steps and ten repeller steps.

With ammonium acetate as additive to the sample solution and with the other additives a discharge voltage of 1500–2000 V was found to favour the ionization process. From these results we conclude that a repeller voltage of −20 V and a discharge voltage of 1750 V with ammonium acetate (see also the asterisk in Fig. 3) as sample solution give the best results and should be used

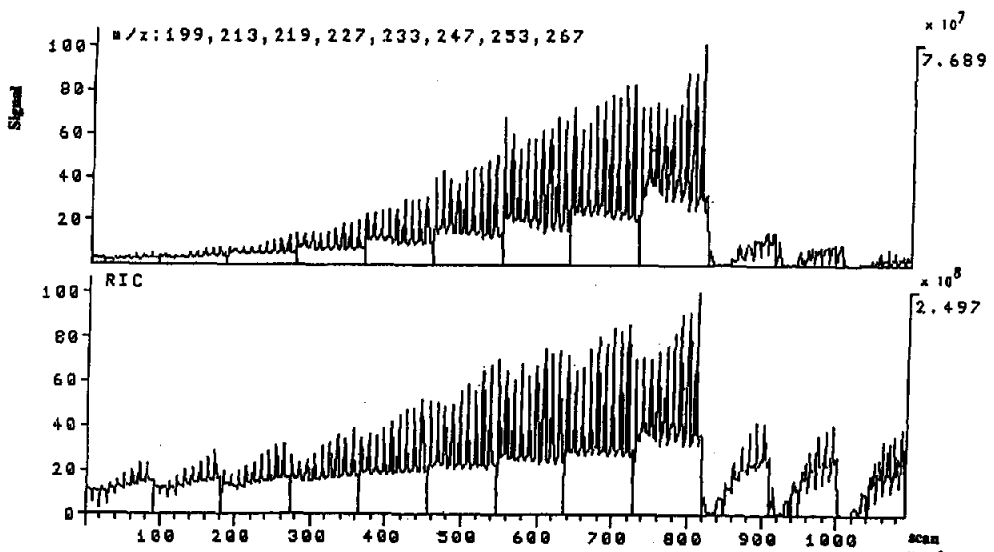

Fig. 2. The RIC and combined mass trace of 0.1 *M* ammonium acetate–acetonitrile (90:10, v/v) at a source block temperature of 200°C, recorded with Procedure I in the Q3-MS mode; for details, see Experimental.

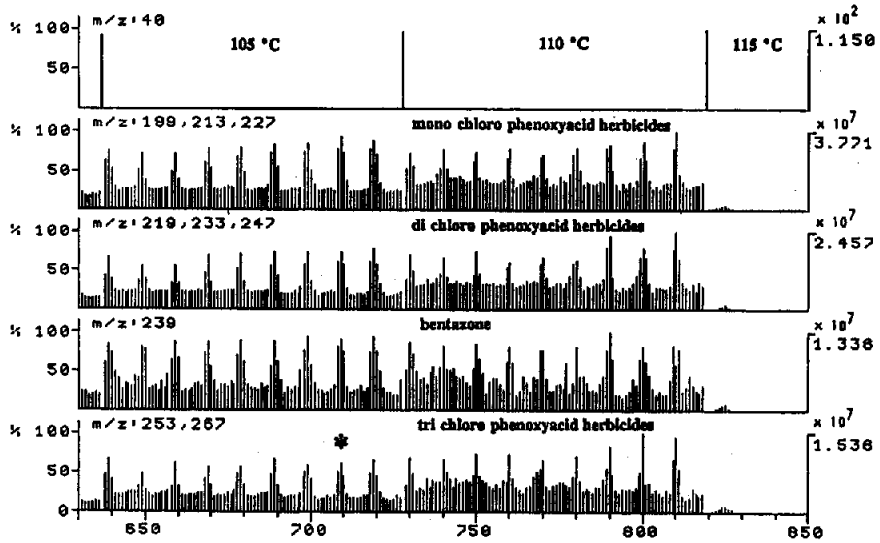

Fig. 3. Expansion of part of the data generated in Procedure I, *viz.*, for vaporizer temperatures of 105, 110 and partly 115°C. The *m/z* 40 trace represents the vaporizer temperature. After every adjustment of the vaporizer temperature the actual source block temperature, aerosol temperature and vaporizer temperature are read out and put as *m/z* 20, 30 and 40, respectively, in the data file for convenient interpretation of the RIC and mass traces. The *m/z* 199, 213, 227 trace represents the combined parent scan masses of MCPA, MCPP and MCPB, respectively. The *m/z* 219, 233, 247 trace represents the combined parent scan masses of 2,4-D, 2,4-DP and 2,4-DB, respectively. The *m/z* 253, 267 trace represents the combined parent scan masses of 2,4,5-T and 2,4,5-TP, respectively. The *m/z* 239 trace represents the parent scan mass of bentazone.

during further optimization according to Procedure II. As an example, a typical result with ammonium acetate is depicted in Fig. 4, selected at a discharge voltage of 1750 V and a repeller voltage of −20 V. As explained under Experimental, the optimum repeller voltage is checked daily.

Collision offset voltage and collision gas pressure

Phenoxyacid herbicides show only slight fragmentation into intense daughter ions. To confirm the identity of the compounds, at least two, and preferably more, ions must be determined, according to mass spectrometric criteria [28]. We therefore decided to select the Cl-35 and Cl-37 isotopes of the molecular ion as the parent scan masses and the Cl-35 and Cl-37 isotopes of the most characteristic fragment as the daughter scan masses. With parent scan mass *m/z* 239 bentazone gave various fragments from which we chose *m/z* 132, 133 and 197 as daughter ion masses.

In Table II the intensities of the daughter ions produced during Procedure II and reported. The results show that at a gas pressure of 3–4 mTorr the daughter-ion signals have the highest intensity. Moreover, for the phenoxyacid herbicides, the measured isotope ratio is good in most instances, which is important for compounds having only one intense fragment and recognition must be based on two data points and their ratio.

At an argon pressure of 3 mTorr the collision offset voltage was, again, increased stepwise from 0 to 30 eV at 1 eV per step. For all phenoxyacid herbicides 18 ± 1 eV turned out to be optimum for producing intense daughter ions, whereas for bentazone 22 ±1 eV was the optimum value.

In order to obtain maximum sensitivity, the combined results of Procedures I and II were used in a multiple reaction monitoring (MRM) method in which two parent ion–daughter ion pairs were monitored for each analyte except for bentazone, for which one parent ion and three

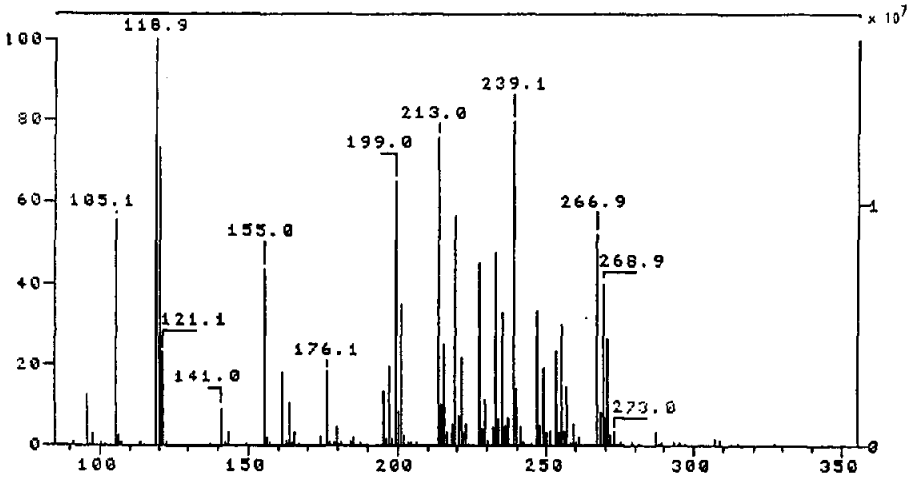

Fig. 4. Spectrum derived from Fig. 3 (see asterisk in Fig. 3) under optimum conditions of Procedure I in the Q3-MS mode. Vaporizer temperature 105°C, discharge voltage 1750 V and repeller voltage −20 V with 0.1 *M* ammonium acetate–acetonitrile (90:10, v/v) at a source block temperature of 200°C.

TABLE II

INTENSITIES ($\times 10^6$) OF DAUGHTER IONS OF PHENOXYACID HERBICIDES AND BENTAZONE

Sample solution, 0.1 *M* ammonium acetate–acetonitrile (90:10, v/v); source block temperature, 200°C; Vaporizer temperature, 105°C; discharge voltage, 1750 V; repeller voltage, −20 V; Flow-rate, 1.5 ml/min; concentration, 50 μg/l of each analyte.

Analyte	Parent ion mass	Daughter ion mass	Intensity				
			1 mTorr	2 mTorr	3 mTorr	4 mTorr	5 mTorr
MCPA	199	141	1.1	3.0	3.2	3.2	2.6
	201	143	0.4	0.9	1.0	1.0	0.9
MCPP	213	141	1.4	2.7	3.2	3.5	2.9
	215	143	0.5	0.8	1.2	1.2	0.9
2,4-D	219	161	0.6	1.3	1.3	1.4	1.4
	221	163	0.4	0.8	1.1	1.1	0.9
MCPB	227	141	0.9	1.4	1.4	1.7	1.2
	229	143	0.3	0.7	0.5	0.6	0.4
2,4-DP	233	161	0.9	1.4	1.5	1.4	1.3
	235	163	0.5	0.9	1.0	1.0	0.8
2,4-DB	247	161	0.4	0.5	0.5	0.5	0.4
	249	163	0.3	0.3	0.3	0.3	0.2
2,4,5-T	253	195	0.3	0.4	0.5	0.5	0.4
	255	197	0.2	0.4	0.5	0.4	0.4
2,4,5-TP	267	195	0.5	0.8	1.1	1.1	0.9
	269	197	0.5	0.8	0.9	0.9	0.8
Bentazone	239	132	0.2	0.8	1.1	1.5	1.2
		133	0.07	0.3	0.4	0.6	0.4
		197	0.08	0.5	0.5	0.7	0.6

TABLE III

SCHEMATIC REPRESENTATION OF MRM PROCEDURE FOR PHENOXYACID HERBICIDES AND BENTAZONE IN MS–MS MODE

collision offset voltage = 18	
psm 199; go 141; psm 201; go 143; stop	**#MCPA**
psm 213; go 141; psm 215; go 143; stop	**#MCPP**
psm 219; go 161; psm 221; go 163; stop	**#2,4-D**
psm 227; go 141; psm 229; go 143; stop	**#MCPB**
psm 233; go 161; psm 235; go 163; stop	**#2,4-DP**
psm 247; go 161; psm 249; go 163; stop	**#2,4-DB**
psm 253; go 195; psm 255; go 197; stop	**#2,4,5-T**
psm 267; go 195; psm 269; go 197; stop	**#2,4,5-TP**
collision offset voltage = 22	
psm 239; go 132; go 133; go 197; stop	**#Bentazone**

daughter ions were selected. This final procedure takes *ca.* 20 s for a complete cycle with a scan time of 1 s for a daughter ion of a selected parent scan mass. This run program is briefly explained in Table III.

Application

First, calibration graphs were constructed using standard solutions in a 0.1 *M* ammonium acetate–acetonitrile (90:10, (v/v) containing 0.125–50 μg/l of each analyte. The results in Table IV show that, without trace enrichment, all phenoxyacid herbicides and bentazone can be determined down to *ca.* 1 μg/l in aqueous standard solutions. The calibration graphs show good linearity over the two orders of magnitude studied. For real drinking and surface water samples, the analytical results will no doubt be less good and trace enrichment of the analytes will have to be performed in order to meet the

TABLE IV

CALIBRATION GRAPH RESULTS OF PHENOXYACID HERBICIDES AND BENTAZONE IN MILLI-Q-PURIFIED WATER

Analyte	Daughter ion mass	r^2	$y = bx + c^a$	Detection limit (3σ) (μg/l)
Bentazone	132.0	0.99994	$y = 4.145x - 0.371$	0.5
	133.0	0.99982	$y = 2.191x - 0.670$	1.0
	197.0	0.99961	$y = 3.542x - 1.334$	1.4
MCPA	141.0	0.99977	$y = 6.367x + 2.026$	1.0
	143.0	0.99996	$y = 2.398x + 0.099$	0.5
MCPP	141.0	0.99850	$y = 7.621x + 3.956$	2.6
	143.0	0.99992	$y = 2.790x - 0.588$	0.7
MCPB	141.0	0.99991	$y = 2.211x + 0.530$	0.7
	143.0	0.99978	$y = 0.784x + 0.009$	1.1
2,4-D	161.0	0.99989	$y = 3.790x + 0.417$	0.7
	163.0	0.99933	$y = 2.611x - 0.792$	1.9
2,4-DP	161.0	0.99991	$y = 5.683x - 0.119$	0.6
	163.0	0.99976	$y = 3.507x - 0.533$	1.2
2,4-DB	161.0	0.99998	$y = 2.303x - 0.179$	0.3
	163.0	0.99988	$y = 1.470x - 0.543$	1.0
2,4,5-T	195.0	0.99981	$y = 2.154x + 0.203$	0.8
	197.0	0.99957	$y = 1.957x + 0.048$	1.4
2,4,5-TP	195.0	0.99999	$y = 6.177x + 0.199$	0.2
	197.0	0.99991	$y = 6.344x - 0.384$	0.6

[a] x = concentration in μg/l; y = intensity (×1000).

EC drinking water regulations, which require a detection limit of 0.1 μg/l for individual pesticides. This can be achieved by an off-line solid-phase extraction of at least 100 ml of sample, desorption with 1 ml of acetonitrile and dilution to 10 ml with 0.1 *M* ammonium acetate. The final sample solution will then have the same composition as the samples in the optimization procedure.

In order to demonstrate the practicability of the present procedure, a surface water sample that contained *ca.* 300 μg/l of bentazone and no phenoxyacid herbicides, as determined by means of LC–UV detection according to a previously described method [3,4], was analysed. After tenfold dilution with Milli-Q-purified water, addition of 10% of acetonitrile and sufficient ammonium acetate to give a 0.1 *M* concentration, the sample was subjected to FIA–TSP-MS–MS. The reconstructed ion chromatogram (RIC) and *m/z* 197 and 132 mass traces in Fig. 5A (standard) and B (surface water sample) show that, with a single 5-ml loop injection, up to 6–8 analysis cycles (scans 60–140) are generated with signals of at least 70% relative intensity which can be used for determination. It can also be seen that the daughter ion of *m/z* 197 (from 2,4,5-T, 2,4,5-TP and bentazone; see also Table III) is present three times in the standard solution and only once (from bentazone) in the

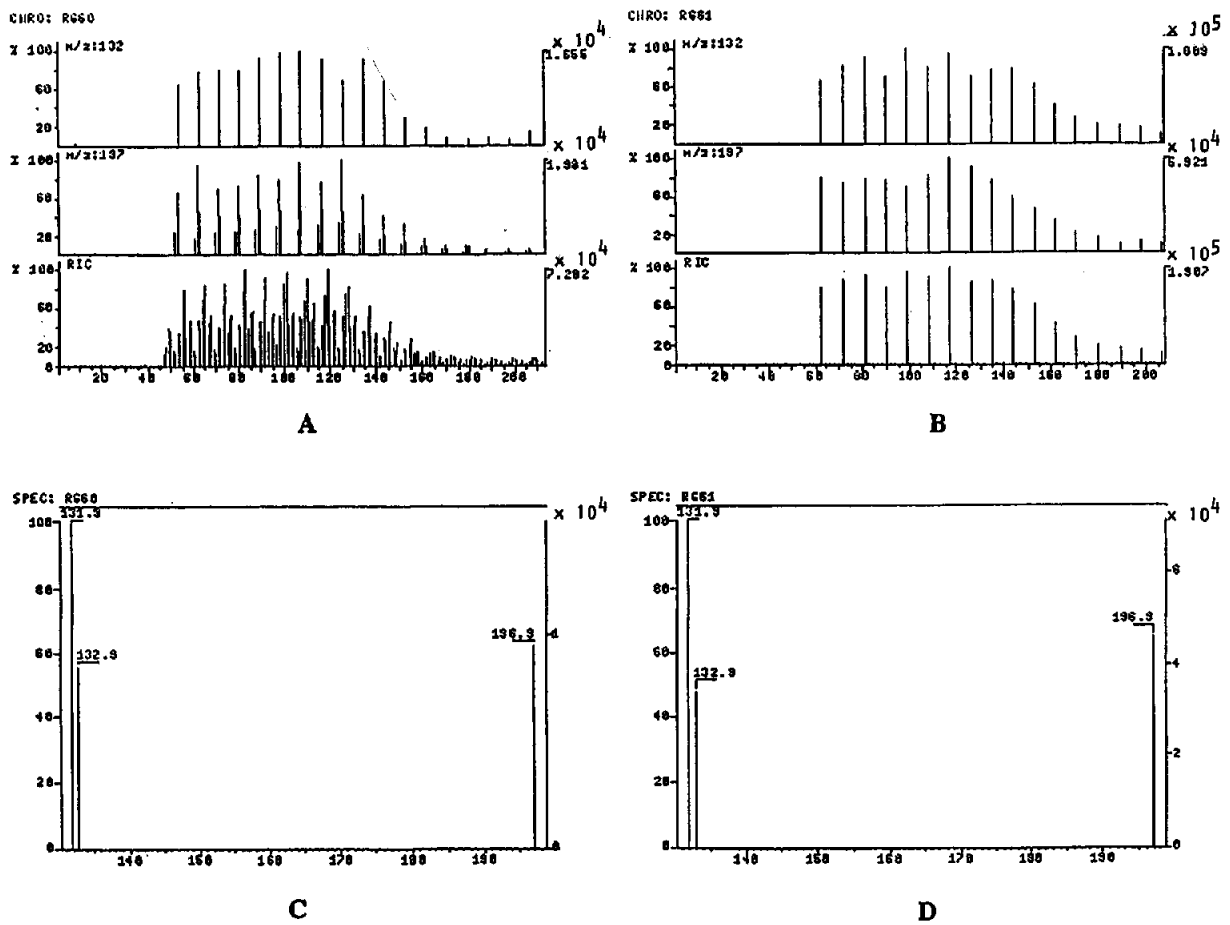

Fig. 5. Chromatogram and spectrum of a 5-ml loop injection of (A and C) a standard sample containing eight phenoxyacid herbicides and bentazone at 5 μg/l and (B and D) a surface water sample after tenfold dilution with MRM procedure (see Table III). Conditions as in Fig. 4.

surface water sample. Fig. 5C (standard) and D (surface water sample) show the resulting mass spectra from the standard and the sample. From their signal intensities the bentazone concentration in the sample was calculated to be 275 μg/l, which agrees satisfactorily with the value quoted above. In addition, as none of the daughter ion masses of the phenoxyacid herbicides were recorded, it can be concluded that, at the low μg/l level, no such herbicides were present. Again, this is in agreement with the LC–UV data quoted above.

CONCLUSIONS

A rapid screening method based on FIA–TSP-MS–MS was developed to detect the presence of phenoxyacid herbicides and bentazone in aqueous samples. With a scan time of 1 s for the daughter ion mass of a selected parent ion mass, a cycle takes 20 s. With a 5-ml loop injection, the total time of analysis, which includes two cleaning steps, is 10 min. Using a multiple reaction monitoring (MRM) method, which is the result of several optimization procedures, one can determine the pesticides at levels down to 1 μg/l in standard solutions without any trace enrichment. For a number of compounds mentioned in the Third National Policy Document on Water Management [1], such detection limits will be good enough. If divergent types of real water samples have to be analysed and the detection limits have to be as low as 0.1 μg/l for individual pesticides, off-line trace enrichment by means of solid-phase extraction with subsequent dilution with a small volume of acetonitrile and appropriate dilution with water may well provide a solution.

The practicability of the proposed method was demonstrated by re-analysing a surface water sample that had already been subjected to LC–UV analysis. In actual practice, however, FIA–TSP-MS–MS will be used for a first rapid screening, with further analysis of suspected samples only by LC-based methods. This approach will considerably increase the speed of analysis and reduce costs.

With a Finnigan TSQ-70 or another, similar, MS–MS instrument the present technique can be used for a broad range of compounds, provided that they can all be analysed at approximately the same source block temperature and collision gas pressure. The more important parameters such as vaporizer temperature, repeller voltage and collision offset voltage can, however, be rapidly adjusted by means of the data system.

REFERENCES

1 *Water in The Netherlands: a Time for Action. Third National Policy Document on Water Management*, Ministry of Transport and Public Works, The Hague, 1989.
2 *EEC Drinking Water Guideline 80/778/EEC, EEC N.L.*, 229 (1980) 11.
3 R.B. Geerdink, C.A.A. van Balkom and H.-J. Brouwer, *J. Chromatogr.*, 481 (1989) 275–285.
4 B.B. Geerdink, A.M.B.C. Graumans and J. Viveen, *J. Chromatogr.*, 547 (1991) 478–483.
5 R.B. Geerdink, F.A. Maris, G.J. de Jong, R.W. Frei and U.A.Th. Brinkman, *J. Chromatogr.*, 394 (1987) 51–64.
6 M.A. Brown, R.D. Stephens and I.S. Kim, *Trends Anal. Chem.*, 10 (1991) 330–336.
7 I.S. Kim, F.I. Sasinos, R.B. Stephens, J. Wang and M.A. Brown, *Anal. Chem.*, 63 (1991) 819–823.
8 D. Barcelo, G. Durand, R.J. Vreeken, G.J. De Jong, H. Lingeman and U.A.Th. Brinkman, *J. Chromatogr.*, 553 (1991) 311–328.
9 D. Barcelo, *Org. Mass Spectrom.*, 24 (1989) 219–224.
10 D. Barcelo, *Org. Mass Spectorm.*, 24 (1989) 898–902.
11 R.D. Voyksner, W.H. McFadden and S.A. Lammert, in J.D. Rosen (Editor), *Applications of New Mass Spectrometry Techniques in Presticide Chemistry*, Wiley, New York, 1987, Ch. 17.
12 D. Barcelo, in M.A. Brown (Editor), *Liquid Chromatography/Mass Spectrometry —Applications in Agricultural, Pharmaceutical and Environmental Chemistry (ACS Symposium Series*, No. 420), American Chemical Society, Washington, DC, 1990, pp. 48–61.
13 T.L. Jones, L.D. Betowski and J. Yinon, in M.A. Brown (Editor), *Liquid Chromatography/Mass Spectrometry —Applications in Agricultural, Pharmaceutical and Environmental Chemistry (ACS Symposium Series*, No. 420), American Chemical Society, Washington, DC, 1990, pp. 62–74.
14 R.J. Vreeken, U.A.Th. Brinkman, G.J. de Jong and D. Barcelo, *Biomed. Environ. Mass Spectrom.*, 19 (1990) 481–492.
15 F.W. McLafferty, in J.F.J. Todd (Editor), *Advances in Mass Spectrometry*, Wiley, New York, 1986, p. 493.
16 T. Cairns and E.G. Siegmund, in M.A. Brown (Editor), *Liquid Chromatography/Mass Spectrometry —Applications in Agricultural, Pharmaceutical and Environmental Chemistry (ACS Symposium Series*, No. 420), American Chemical Society, Washington, DC, 1990, pp. 40–47.
17 K.S. Chiu, A. Van Langenhove and C. Tanaka, *Biomed. Environ. Mass Spectrom.*, 18 (1989) 200–206.

18 L.D. Betowski and T.L. Jones, *Environ. Sci. Technol.*, 22 (1988) 1430–1434.
19 H.F. Schröder, *J. Chromatogr.*, 554 (1991) 251–266.
20 S.V. Hummel and R.A. Yost, *Org. Mass Spectrom.*, 21 (1986) 785–791.
21 H.F. Schröder, *Water Sci. Technol.*, 23 (1991) 339–347.
22 H.F. Schröder, *Wasser*, 73 (1989) 111–136.
23 D.F. Hunt, *Anal. Chem.*, 57 (1985) 525–537.
24 L.D. Betowski, S.M. Pyle, J.M. Ballard and G.M. Shaul, *Biomed. Environ. Mass Spectrom.*, 18 (1987) 343–354.
25 K.L. Busch, G.L. Glish and S.A. McLuckey (Editors), *Mass Spectrometry/Mass Spectrometry, Techniques and Applications of Tandem Mass Spectrometry*, VCH, New York, 1988.
26 J.V. Johnson and R.A. Yost, *Anal. Chem.*, 57 (1985) 758A–768A.
27 S.D. Menacherry and J.B. Justice, Jr., *Anal. Chem.*, 62 (1990) 597–601.
28 *Off. J. Eur. Commun.*, L223 (1987) 26.