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Determination of chlorophenoxy acid herbicides in water by in situ esterification followed by in-vial liquid–liquid extraction combined with large-volume on-column injection and gas chromatography–mass spectrometry

M. Isabel Catalina*, Jens Dallüge, René J.J. Vreuls, Udo A.Th. Brinkman

Vrije Universiteit, Department of Analytical Chemistry and Applied Spectroscopy, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract

A new approach for rapidly analysing chlorophenoxy acid herbicides in water is presented. The chlorinated acids are derivatised with dimethyl sulphate in the water sample itself (800 μl) and, next, the methyl esters are extracted with 800 μl of *n*-hexane. A 200-μl volume of the extract is injected into the GC–MS system. The miniaturisation of both the methylation and extraction steps could be implemented because of the use of large-volume on-column injection and mass spectrometric detection. The optimisation of the methylation reaction for the simultaneous determination of (3,6-dichloro-2-methoxy)benzoic acid, (2-methyl-4-chlorophenoxy)- and (2,4-dichlorophenoxy)acetic acids, (±)-2-(4-chloro-2-methylphenoxy)- and 2-(2,4-dichlorophenoxy)propanoic acids and 4-(4-chloro-2-methylphenoxy)- and 4-(2,4-dichlorophenoxy)butyric acids showed that tetrabutylammonium salts act as catalysts. Addition of sodium hydroxide was required to obtain quantitative reaction yields for 4-(4-chloro-2-methylphenoxy)- and 4-(2,4-dichlorophenoxy)butyric acids. The methylation-cum-extraction procedure takes only 3 min per sample for a batch of seven samples. Linear calibration plots were obtained for the complete procedure and the limits of detection were of 10–60 ng/l with a signal-to-noise ratio (S/N) of 6. Relative standard deviations ranged from 8 to 15% (n=7) for analyte concentrations of 0.5 μg/l in surface water.

Keywords: Water analysis; Environmental analysis; Large-volume injection; Derivatization, GC; Extraction methods; Chlorophenoxy acids; Phenoxy acids; Pesticides; Dimethyl sulphate

1. Introduction

Chlorinated phenoxy acids are selective agricultural herbicides which are widely used to control broad-leaved weeds and other vegetation. They are inexpensive and very potent even at low concentrations [1]. Because of their high water solubility and toxicological risk, monitoring of ground and drinking water for their presence is required.

The determination of these compounds by gas chromatography (GC) is complicated due to their

*Corresponding author.

E-mail address: catalina@chem.vu.nl (M.I. Catalina)

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low volatility caused by the hydrogen bonding of their carboxylic acid and phenol functionalities. Furthermore, because of their polar nature, they are adsorbed on the GC stationary phase which causes peak asymmetry. Therefore, masking of these polar groups by derivatization to their corresponding esters is needed in order to yield products that can undergo analysis by GC [2].

Among the different derivatization methods, such as silylation, esterification and alkylation, silylation is considered unsatisfactory for trace-level analysis because the sensitivity generally achieved with the silyl derivatives is not high enough [3]. Moreover, the reaction requires temperatures of about 50°C and reaction times of some 4 h using, for example, a mixture of *N*,*O*-bis(trimethylsilyl)acetamide-trimethylchlorosilane (80:20) [2]. For alkylation or haloalkylation a very extensive list of reagents exists among which diazomethane, alkyl and haloalkyl halides (e.g., methyl iodide, benzyl bromide and pentafluorobenzyl bromide), alcohols and halogenated alcohols (e.g., methanol and 2,2,2-trifluoroethanol using acid catalysts) are the most common ones. Diazomethane is the most frequently used derivatization agent for phenoxy acids. It is applied in US Environmental Protection Agency (EPA) Methods 515.3 and 8151 for the determination of chlorinated acids in drinking water, and water, soil and waste samples, respectively [4,5]. Nevertheless, the whole sample preparation procedure required when using diazomethane for methylation, i.e., formation of diazomethane from its precursors, clean-up after methylation, etc., is highly laborious and time-consuming. Besides, due to hazard risks regarding toxicity, carcinogenity and the danger of explosions, alternative routes are eagerly sought [6].

Generally, prior to the determination of acidic compounds in water, the analytes are transferred to an organic matrix where alkylation takes place. Only a few studies consider the option of performing the methylation directly in the water matrix [7,8]. Recently, the use of dimethyl sulphate (DMS) as derivatization agent in water for halo-acetic acids in static headspace techniques has been reported. In this case, ion-pairing agents such as tetrabutylammonium (TBA) salts were used as, what is thought to be, strong modifiers to activate the analytes during the in situ methylation process [9].

Systems that use DMS and ion-pairing agents (onium salts) are well known in liquid–liquid phase-transfer catalysis, where the analytes are dissolved in the organic phase together with the ion-pairing agent which acts as catalyst that promotes the transfer of the analytes into the water phase where DMS is present and the derivatization reaction occurs [10]. Ammonium salts have rarely been considered as promoters or catalyst in one-phase aqueous systems.

This study focuses on the optimisation of the methylation reaction with subsequent in-vial liquid–liquid extraction of several chlorophenoxy acid herbicides (see Fig. 1), using DMS for methylation and tetrabutylammonium salts as ion-pairing agent. Moreover, the influence of sodium sulphate added to the reaction matrix at or above the saturation level during both methylation (pH regulation) and extraction (fast phase separation, salting-out effect) is investigated.

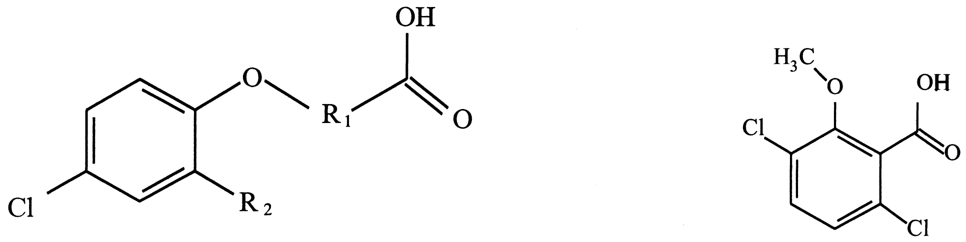
The injection of a large aliquot of the final extract, viz. 25% or 200 μl, and the use of selective and sensitive mass spectrometric detection, allowed a rigorous miniaturisation of the sample preparation procedure such that it could be performed in an autosampler vial. The miniaturised procedure of in situ methylation and in-vial liquid–liquid extraction allowed the determination of the acid herbicides with detection limits below the μg/l level and created possibilities of performing the procedure at-line with GC–mass spectrometry (MS).

2. Experimental

2.1. Standards and reagents

The seven phenoxy alkanoic acids (see Fig. 1) and their methyl esters, were purchased from Riedel-de Haën (Seelze, Germany). Standard solutions of individual compounds were prepared in acetonitrile at 1 g/l. Two standard mixtures containing either all the acids or their methyl esters were prepared by suitable dilution to a final concentration of 400 μg/l in methyl acetate.

n-Hexane, acetonitrile and methyl acetate were purchased from J.T. Baker (Deventer, The Netherlands) and were freshly distilled before use. Sodium sulphate (anhydrous) and sodium hydroxide (pellets)



Dicamba

Phenoxy acids (IUPAC name)	R_1	R_2
MCPP (+/-)-2-(4-chloro-2-methylphenoxy) propanoic acid	$-CH-CH_3-$	$-CH_3$
MCPA (2-methyl-4-chlorophenoxy) acetic acid	$-CH_2-$	$-CH_3$
2,4-DP 2-(2,4-dichlorophenoxy) propanoic acid	$-CH-CH_3-$	$-Cl$
2,4-D (2,4-dichlorophenoxy) acetic acid	$-CH_2-$	$-Cl$
MCPB 4-(4-chloro-2-methylphenoxy) butyric acid	$-CH_2-CH_2-CH_2-$	$-CH_3$
2,4-DB 4-(2,4-dichlorophenoxy) butyric acid	$-CH_2-CH_2-CH_2-$	$-Cl$
Dicamba (3,6-dichloro-2-methoxy) benzoic acid		

Fig. 1. Structures of the acid herbicides used in the study.

were also purchased from Baker. Two TBA salts, TBA hydroxide and TBA hydrogensulphate, as well as the methylation reagent, DMS, were obtained from Åcros (Geel, Belgium). 4,4′-Difluorobiphenyl (Sigma–Aldrich, Steinheim, Germany) was used as internal standard. HPLC-grade water was prepared by means of quartz distillation of Milli-Q grade water.

2.2. *In situ esterification and in-vial liquid–liquid extraction*

2.2.1. *Optimisation of the aqueous-phase derivatization*

The miniaturised procedure was carried out by analysing 800-μl water samples in 1.8-ml autosampler vials. For the optimisation of the derivatization conditions, standard water samples were prepared by spiking all the acid herbicides at the 2 μg/l level. In all cases 8 μl of DMS was added. Depending on the parameter under investigation, additional reagents were added to promote the DMS action as methylating agent. The following parameters were studied:

Addition of tetrabutylammonium salts. Both TBA hydrogensulphate and TBA hydroxide were used to enhance the methylation yield and to select the best initial pH conditions (basic for hydroxide or neutral for hydrogensulphate as counterion, respectively). Prior to the start of the derivatization reaction by means of adding DMS, 8 μl out of an aqueous solution of 80 mg/ml TBA salt was added to an aqueous sample to study the role of the TBA salts as promoters of the reaction.

Addition of sodium sulphate. The influence of sodium sulphate, approx. 300 mg, which is far above the saturation level, were added to the 800-μl water sample prior to the addition of the TBA salt and DMS.

Influence of pH. In order to monitor the pH during the derivatization reaction, 5-ml samples were analysed in 20-ml screw-capped vials. Accordingly, the amounts of both DMS and TBA salt solution were increased to 50 μl. After a reaction time of 3 min, the pH was adjusted by adding various amounts of sodium hydroxide. A combi-glass electrode (Metrohm, Herisau, Switzerland) was used for the pH measurements.

Reaction time. The derivatization time was varied from 3 to 30 min at ambient temperature.

2.2.2. In-vial liquid–liquid extraction

After the aqueous-phase methylation of the acids, the corresponding esters were extracted with an equal amount of *n*-hexane. The extraction solvent contained 4,4′-difluorobiphenyl as internal standard (I.S.) at a concentration of 10 ng/ml. The two-phase system was vigorously stirred for a few seconds using a vortex mixer. The influence of sodium sulphate to promote the extraction efficiency by the salting-out effect was studied in some detail. The extraction yields of the methyl esters were calculated using standard solutions of the methyl esters as reference.

2.3. Instrumentation: GC–MS

2.3.1. Set-up of large-volume injection-GC system

All extracts were analysed using a large-volume injection (LVI)-GC system as illustrated in Fig. 2. It consisted of a Carlo Erba Series 8000 gas chromatograph equipped with an on-column injector and an MD 800 mass spectrometer (CE Instruments, Milan, Italy). A Model F101D-HA flow meter (0–200 ml/min range; Bronkhorst, Ruurlo, The Netherlands) was inserted into the carrier gas supply line between the pressure regulator and the on-column injector. Its output (0–5 V) was used to monitor the evaporation process and to control the solvent vapour exit valve. The solvent vapour exit, which is opened and closed by an electronically controlled three-port valve (CE Instruments), was installed directly after the retention gap via a glass Y-piece and was controlled by the microprocessor-based controller. Description of the controller features as well as the procedures for the fast optimisation of the automated solvent vapour exit closure time for the on-column LVI using this set-up, has been described in detail in recent papers [11,12]. Both a 5-m diphenyltetramethyldisilazane-deactivated retention gap (0.53 mm I.D.; BGB Analytik, Zurich, Switzerland) and a 30-m analytical column (DB-XLB, 0.25 mm I.D., film thickness 0.25 μm; J&W, Folsom, CA, USA) were also connected to the glass Y-piece. Helium 5.0 (Hoekloos, Schiedam, The Netherlands) was the carrier gas. All injections were carried out at the standard boiling point of *n*-hexane, 69°C, and 150 kPa head pressure.

Out of each 800-μl *n*-hexane extract, 200 μl was

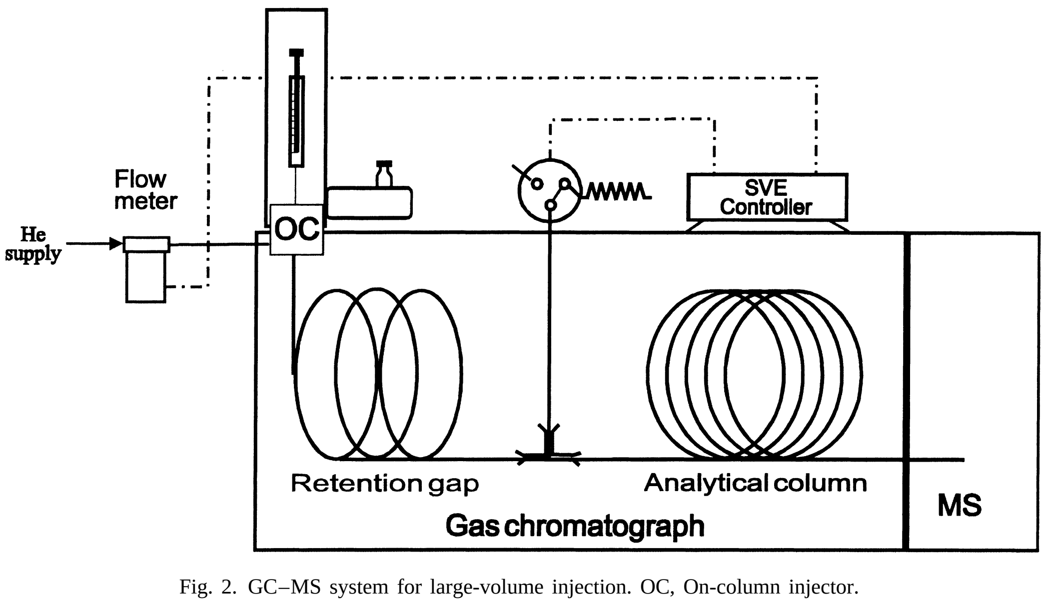


Fig. 2. GC–MS system for large-volume injection. OC, On-column injector.

injected on-column into the gas chromatograph at a speed of 4 μl/s. For this liquid–liquid extraction–LVI-GC–MS analysis of aqueous samples, an AS 800 autosampler (CE Instruments) with a 250-μl syringe was used.

After the automated closure of the solvent vapour exit detected by the controller at about 17 s after the end of the injection, the temperature-programmed analysis was started using an oven temperature programme from 69°C (1 min) at 10°C/min to 285°C (5 min).

2.3.2. MS detection

The mass spectrometer was operated in the electron ionisation mode. Two modes of operation were used, i.e., full-scan acquisition in the range 50–450 m/z in 0.50 s, and selected ion recording (SIR) using a dwell-time of 0.08 s and an inter-channel delay of 0.02 s. Ions recorded in the SIR mode are listed in Table 1. The base ions were used for quantification purposes.

2.4. Quantification: total yields and linearity

To determine the yield of the acid herbicides in the complete procedure, i.e., after both methylation and liquid–liquid extraction, the peak areas of each methylated acid herbicide were divided by that of the internal standard and compared to the standard esters in *n*-hexane at the same level. Prior to and/or after a series of experiments at a certain concentration level, a sequence of 3–5 standard injections was performed at the same level in order to calculate the total yields.

The peak area-ratio (I.S. correction) vs. concentration plots were constructed using large-volume on-column injection of standards in the 0.1–10 μg/l range containing 10 μg/l of the internal standard. Calibration plots contained at least five data points. Standards were prepared by dilution of the stock solution in *n*-hexane and each concentration level was determined in triplicate.

Table 1
Characteristic ions for the methyl esters of the phenoxy acid herbicides

Phenoxy acid	m/z recorded in SIR			m/z of other ions
	BI[a]			
Dicamba	203	205	234[b]	236, 188, 160, 175
MCPP	169	228[b]	107	142, 77, 125, 44
MCPA	141	155	214[b]	125, 127, 143, 157, 216
2,4-DP	162	164	248[b]	189, 191, 250
2,4-D	199	175	234[b]	177, 201, 236
MCPB	101	107	213	59, 77, 142, 211, 242[b]
2,4-DB	101	164	231	59, 133, 135, 162, 262[b]

[a] Base ion.
[b] Molecular ion.

3. Results and discussion

Firstly, the injection of 200 μl of *n*-hexane was optimised using the methyl esters of the acid herbicides as test compounds and appropriate detection conditions were selected. Secondly, the influence of salt addition on the extraction of the methyl esters was studied. Finally, several parameters of the derivatization process were optimised by determining the total yields of the whole procedure. Under optimised conditions, total yields, calibration curves and detection limits were determined by using MS detection in the SIR mode. The total procedure was applied to the determination of acid herbicides by injecting 200 μl out of a 800-μl extract into the GC–MS system. Surface and tap water samples were analysed without any pre-treatment, even without filtration.

3.1. Large-volume injection

During the whole study, the evaporation process was monitored by using a solvent vapour exit control box [11]. By measuring changes in the carrier gas flow-rate in the inlet line as depicted in Fig. 3, a microprocessor determined the exact moment in time at which the evaporation process was completed: during solvent evaporation the flow-rate reached a value of about 40 ml/min, while at the end of the evaporation process a very steep increase occurred (indicated by arrow No. 4). The time needed for evaporation (with a precision of 0.2 s) and the steep increase at the end of the process (in ml/min^2) were stored by the microprocessor.

For the selected retention gap, inlet pressure and temperature, an injection speed of at least 4 μl/s was required in order that the evaporation time exceeded the injection time. Under these conditions a solvent film was formed on the inner wall of the retention

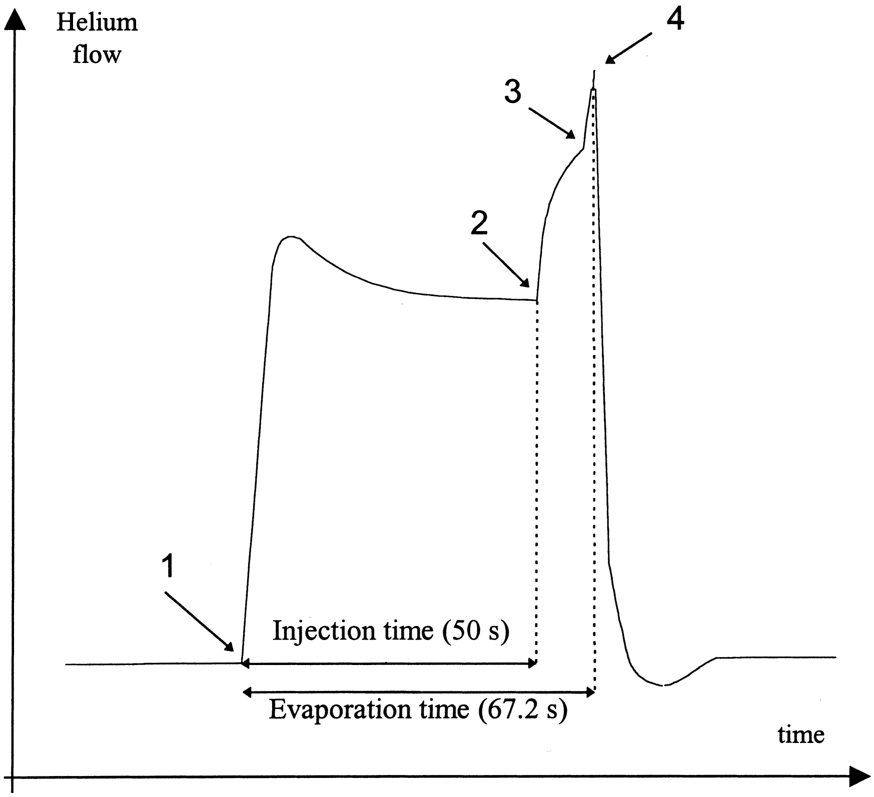


Fig. 3. Helium flow-rate profile obtained during injection of 200 μl of *n*-hexane. Arrows indicate: (1) needle into retention gap, solvent vapour exit open and start of injection at 4 μl/s; (2) end of injection, needle out; (3) end of evaporation process; (4) solvent vapour exit closed.

gap. The controller recorded an evaporation time of 67.2 s for a 50-s injection. Although the phenoxy acid esters are not so volatile that the so-called solvent effect is required, the injection speed was kept above the evaporation rate (4 μl/s injection speed vs. 3.1 μl/s evaporation rate) and the solvent vapour exit was closed at the moment in time at which the flow measurement sensed the end of the evaporation process.

3.2. Liquid–liquid extraction of the methyl esters

To study the extraction of the methyl esters of the acid herbicides from the aqueous phase into *n*-hexane, five extraction replicates of the MCPP, MCPA and 2,4-DB methyl esters spiked into the water phase at 5 ng/ml were performed with and without sodium sulphate being present. In both instances, the extraction yields were calculated by comparison with standards in *n*-hexane at the same ng/ml level. Fig. 4 clearly shows that extraction is nearly complete in both cases. Although extraction yields did not increase, phase separation was much faster when salt was present in the solution. These results imply that deviations from quantitative recovery in the complete derivatization-cum-extraction procedure of the intended method will have to be attributed solely to incomplete derivatization rather than a cumulative effect from both individual steps.

3.3. In situ derivatization

Preliminary experiments in which DMS was added to aqueous solutions containing each of the six test compounds, showed that methylation in the aqueous phase was far from complete. Results are shown as

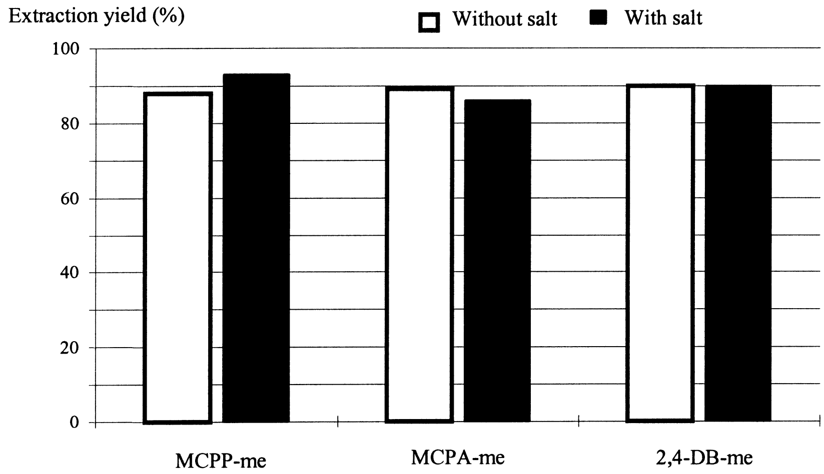


Fig. 4. Extraction yields of three acid herbicide methyl esters with and without addition of sodium sulphate.

black bars in Fig. 5b. The highest (overall) yields were obtained for MCPP (36%) and 2,4-DP (25%), while for the others values below 15% were found. Addition of sodium sulphate resulted in higher yields of up to 70% for MCPP, but the average yield still was no more than about 50% (Fig. 5a, black bars).

The addition of TBA salts (but **no** sodium sulphate) to the water sample did not enhance the total yield to some substantial extent. TBA hydroxide gave significantly higher yields than the TBA hydrogensulphate for the two acids with a propionic acid group, but the overall result was disappointing (Fig. 5b).

Finally, when ion pairing was used in combination with the addition of sodium sulphate, all analytes showed about 30% improved yields, and quantitative recovery was found for three analytes. The addition of TBA hydrogensulphate instead of TBA hydroxide gave a significantly better yield for 2,4-D, but in general terms, the nature of the TBA counterion seemed not to play an essential role in the derivatization itself.

The fact that the two compounds with the highest pK_a value (MCPB and 2,4-DB; see Table 2) had the lowest yields led to the idea that the pH of the solution during the derivatization process played an important role. The presence of the anionic form of the acids appears to be essential, as is common for this type of SN-2 reactions. The role of pH and pH modification was studied in some detail in further experiments.

Table 2
Properties of interest of phenoxy acid herbicides

Phenoxy acid	CAS No.[a]	M_r [b]	pK_a [c]	Log K_{ow} [d] of esters
Dicamba	1918-00-9	220.0	3.27	3.20
MCPP	93-65-2	214.6	3.75	3.22
MCPA	94-74-6	200.6	3.05	2.81
2,4-DP	120-36-5	235.1	3.00	3.03
2,4-D	94-75-7	221.0	2.73	2.90
MCPB	94-81-5	228.7	4.80	3.79
2,4-DB	94-82-6	249.1	5.95	3.89

[a] Chemical Abstract service registry number.
[b] Molecular mass.
[c] −Log (acid–base dissociation constant).
[d] Log (octanol–water partition coefficient) calculated from KOWWIN Program (Syracuse Research Corp.'s octanol–water partition coefficient program, New York, NY, USA).

3.3.1. pH during reaction

When TBA hydroxide was added (50 μl of an aqueous 80 mg/ml solution to 5 ml water), the initial pH of the aqueous solution was about 11.4, while that for the solution containing the same amount of TBA hydrogensulphate was 6.2. Plotting the pH of the various solutions as a function of the reaction time (see Fig. 6) immediately showed that these initial pH values had little relevance. Upon addition of the methylating reagent, the pH dropped almost instantaneously to a value below 2.5 due to acidifica-

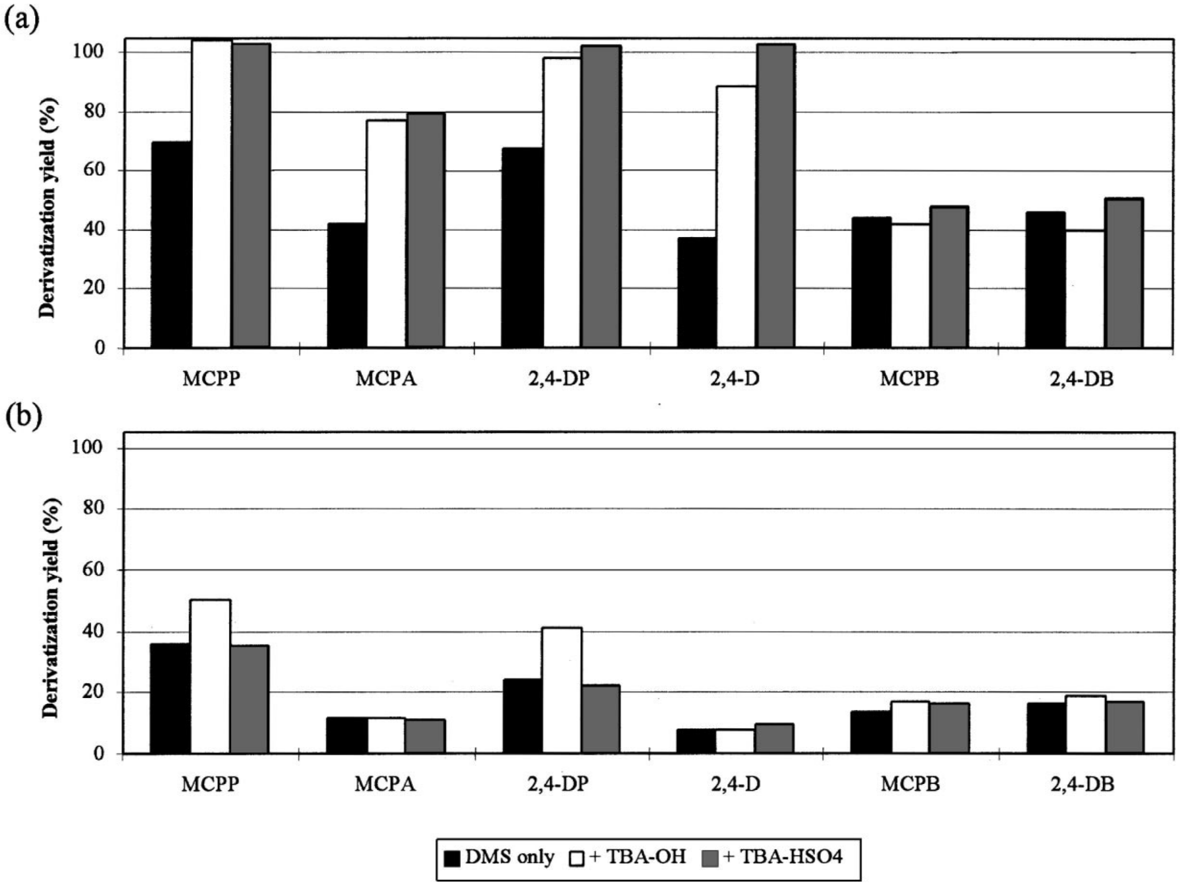


Fig. 5. Derivatization yields of six acid herbicides after in situ methylation and in-vial liquid–liquid extraction (a) with and (b) without addition of sodium sulphate using solely DMS for the reaction, or DMS in combination with either TBA hydroxide or TBA hydrogensulphate.

tion as a result of the DMS hydrolysis, independently of the counterion of the TBA salt. The pH value of the TBA hydroxide-containing solution was 0.2 units higher than for the TBA hydrogensulphate-containing solution. This may explain the somewhat higher derivatization yields when using TBA hydroxide as ion pairing agent (no sodium sulphate present). The higher pH value increases the anion concentration in the acid–anion equilibrium. Since neither the reaction kinetics nor the reaction mechanism have been studied as yet, the above consideration cannot explain why the two herbicides containing a propionic acid group have higher yields than MCPA and 2,4-D, which have either a lower or similar pK_a value.

Fig. 6 also illustrates that the pH value of the solution in which the reaction takes place is significantly higher and decreases more slowly when sodium sulphate in present. Only those analytes with a pK_a value some two units higher than the pH of the solution show incomplete derivatization, which again strongly suggests that the pH during the first few minutes of the reaction is very important.

Concerning the nature of the TBA counterion, TBA hydroxide was chosen because the phenoxy acid herbicides are spread in the fields both in the acidic and alkylated form, and increasing the pH of the initial water sample up to about 12 all the herbicides can be analyzed as the carboxylate form.

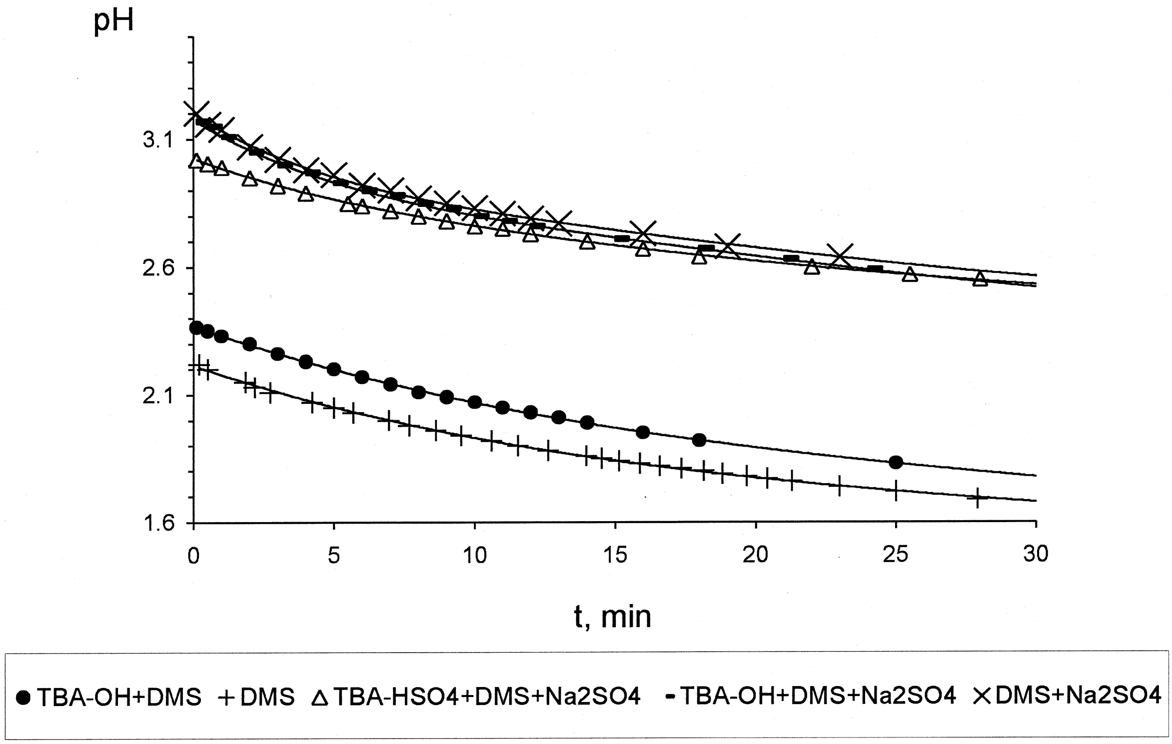


Fig. 6. pH as a function of reaction time in various solutions containing DMS, TBA hydroxide and/or TBA hydrogensulphate with and without addition of sodium sulphate.

3.3.2. Addition of sodium hydroxide during reaction

Since the hydrolysis of DMS by the carboxylate anions [13] of MCPB and 2,4-DB with their high pK_a values (Table 2) was still incomplete, sodium hydroxide was added to promote the quantitative generation of the butyrate forms of these two analytes. From 25 to 4000 μmol of sodium hydroxide was added to 5-ml water samples spiked at 2 μg/l with each of the acid herbicides (TBA hydroxide and DMS present in amounts mentioned above). After 10 min, the esters were extracted with 5 ml of *n*-hexane and, next, 200 μl of these extracts were injected into the GC–MS system. The results for eight different NaOH concentration levels (n=3 per concentration) clearly showed that (i) the two analytes of interest, i.e., MCPB and 2,4-DB, could be quantitatively converted into their corresponding esters and (ii) the yields of the other analytes were not significantly influenced compared to the experiments without addition of sodium hydroxide, when an amount in the range of 100-150 μmol of NaOH was added (Fig. 7).

3.3.3. Reaction time after addition of sodium hydroxide

The time dependence of the reaction yield for the procedure with sodium hydroxide added to the reaction mixture was also studied. To that end, the extractions with *n*-hexane were carried out 3 to 30 min after addition of sodium hydroxide. The results of Fig. 8 clearly demonstrate that the methyl esters of all acid herbicides start to degrade after about 5–10 min, with the degradation being about 20% after 30 min. Recording the pH after the addition of sodium hydroxide showed that the reaction mixture was basic for some 7 min. Thereafter, the hydrolysis of DMS consumed all hydroxide ions and the solution became acidic (Fig. 9) which triggered the hydrolysis of the esters (Fig. 8).

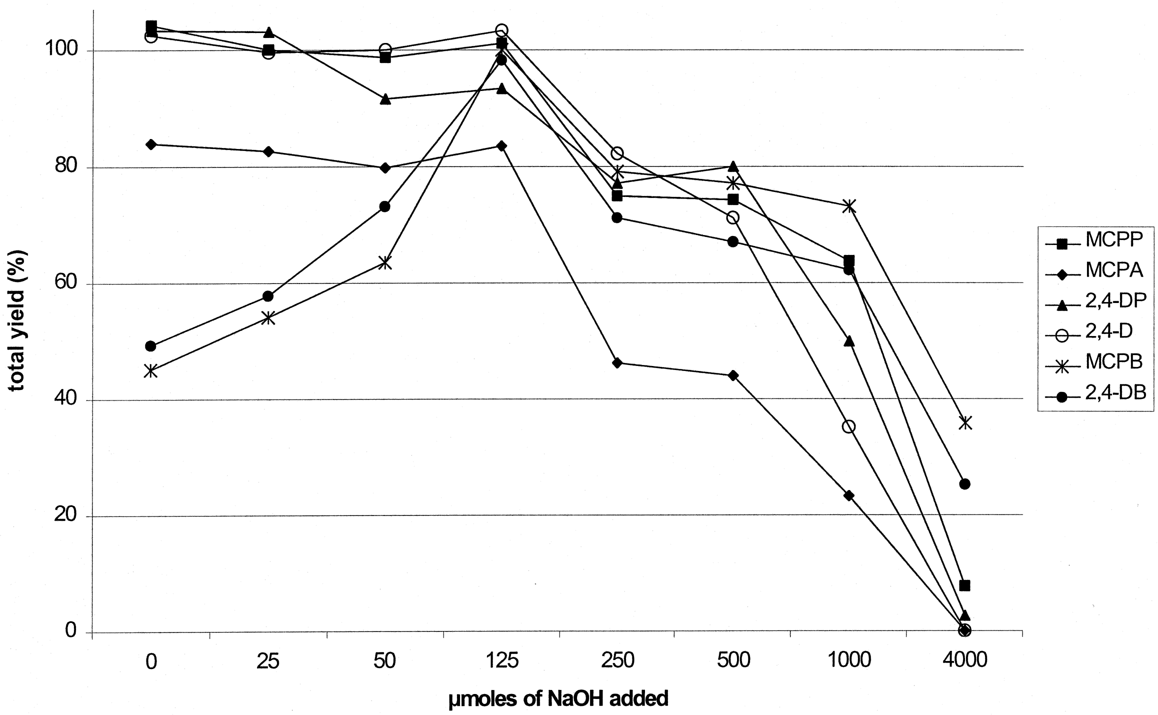


Fig. 7. Influence of amount of NaOH added to the reaction mixture upon the total analyte yield.

3.3.4. Final procedure

The final methylation-cum-extraction procedure can be summarised as follows:

1. 800 μl water samples are pipetted into an autosampler vial
2. 8 μl of a 80 mg/ml-containing TBA hydroxide solution in water are added
3. ca. 300 mg of sodium sulphate (above the saturation level) are added
4. 8 μl of DMS are added to initiate the reaction
5. Vortex mixing for approx. 10 s
6. 4 μl of a 5 *M* sodium hydroxide solution is added
7. Vortex mixing for approx. 10 s
8. After a further 3 min, 800 μl of *n*-hexane is added to extract the methyl esters
9. Vortex mixing for approx. 10 s
10. Vial ready to be placed in autosampler, 200 μl of *n*-hexane extract injected into the GC–MS system.

3.4. Analytical data and application

The above procedure gave rather promising results for acid herbicide analysis. Relative standard deviations at the 0.5 μg/l level ranged from 8 to 15% ($n=7$). All analyte response vs. concentration plots were linear in the 0.1–10 μg/l range (seven data points in triplicate) and detection limits in the SIR mode were between 10 ng/l for dicamba and 60 ng/l for 2,4-DB with a signal-to-noise ratio of 6. Results for all analytes are summarised in Table 3. The procedure was carried out within 3 min per sample using batches of seven samples (estimated during the analysis of the 21 samples for the study of linearity).

Table 3
Analytical data for the phenoxy acid herbicides at 0.5 μg/l level[a]

	m/z	LOD (ng/l)	RSD (%) $n=7$	r^2
Dicamba	234	10	9	0.9998
MCPP	228	25	11	0.9992
MCPA	214	40	10	0.9993
2,4-DP	162	20	9	0.9998
2,4-D	199	60	13	0.9967
MCPB	101	40	15	0.9935
2,4-DB	101	60	8	0.9991

[a] Limits of detection (LODs) for a $S/N=6$.

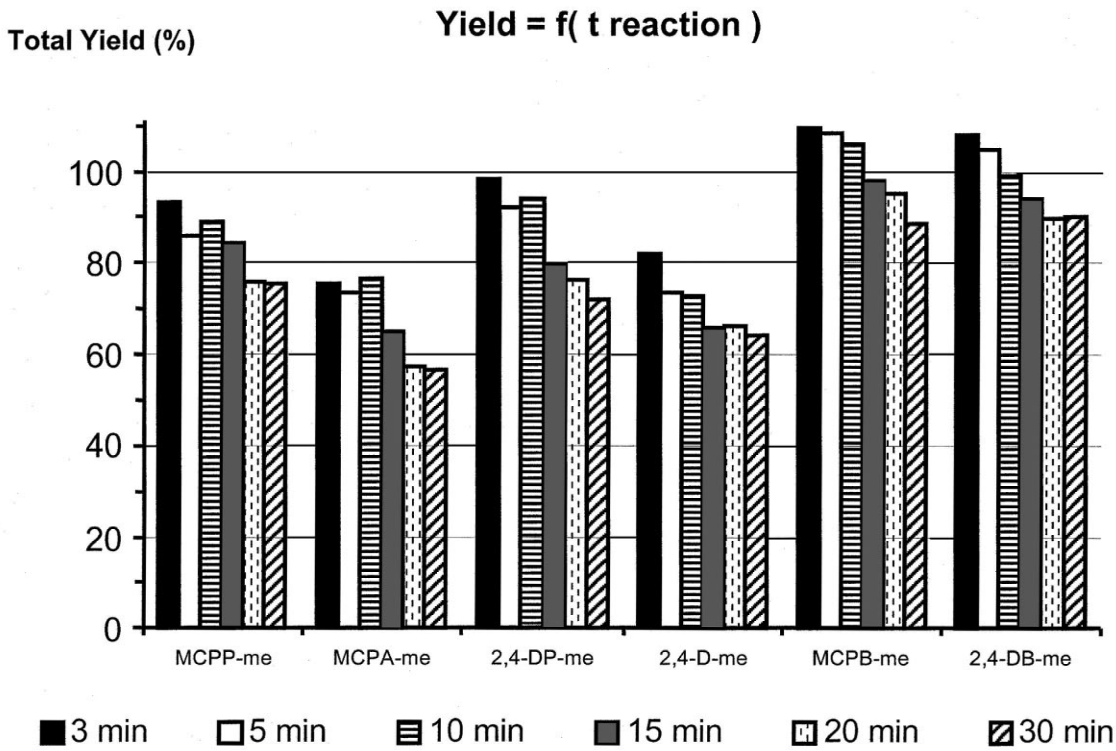


Fig. 8. Analyte yield as function of time elapsed after addition of sodium hydroxide.

As an example, the ion traces for the individual compounds in Figs. 10 and 11 obtained for surface water from the river Rhine spiked with 0.3 μg/l of each dicamba and 2,4-DP, 0.5 μg/l of each MCPP and MCPA, 0.7 μg/l 2,4-DB, 0.9 μg/l MCPB, and 1 μg/l 2,4-D, clearly illustrate the above findings. River Rhine (Lobith, The Netherlands) water was filtered through a 0.45-μm BA membrane filtration system (Schleicher & Schuell, Dassel, Germany). No traces of these phenoxy acid herbicides were found in this Rhine river water sample collected at Lobith (4 August 1999). The target analysis of these herbicides using MS detection in the SIR mode (for m/z recorded, see Table 1) was performed with and without filtration over a 0.45-μm filter: no significant differences were observed between the SIR chromatograms.

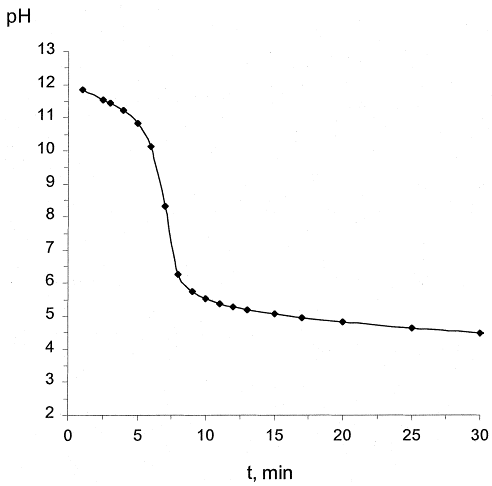


Fig. 9. Change of pH during methylation reaction after addition of 125 μmol of NaOH.

4. Conclusions

A rapid and straightforward sample handling procedure for phenoxy acids in water has been developed, with subsequent GC–MS analysis. Although there is no sample enrichment in this

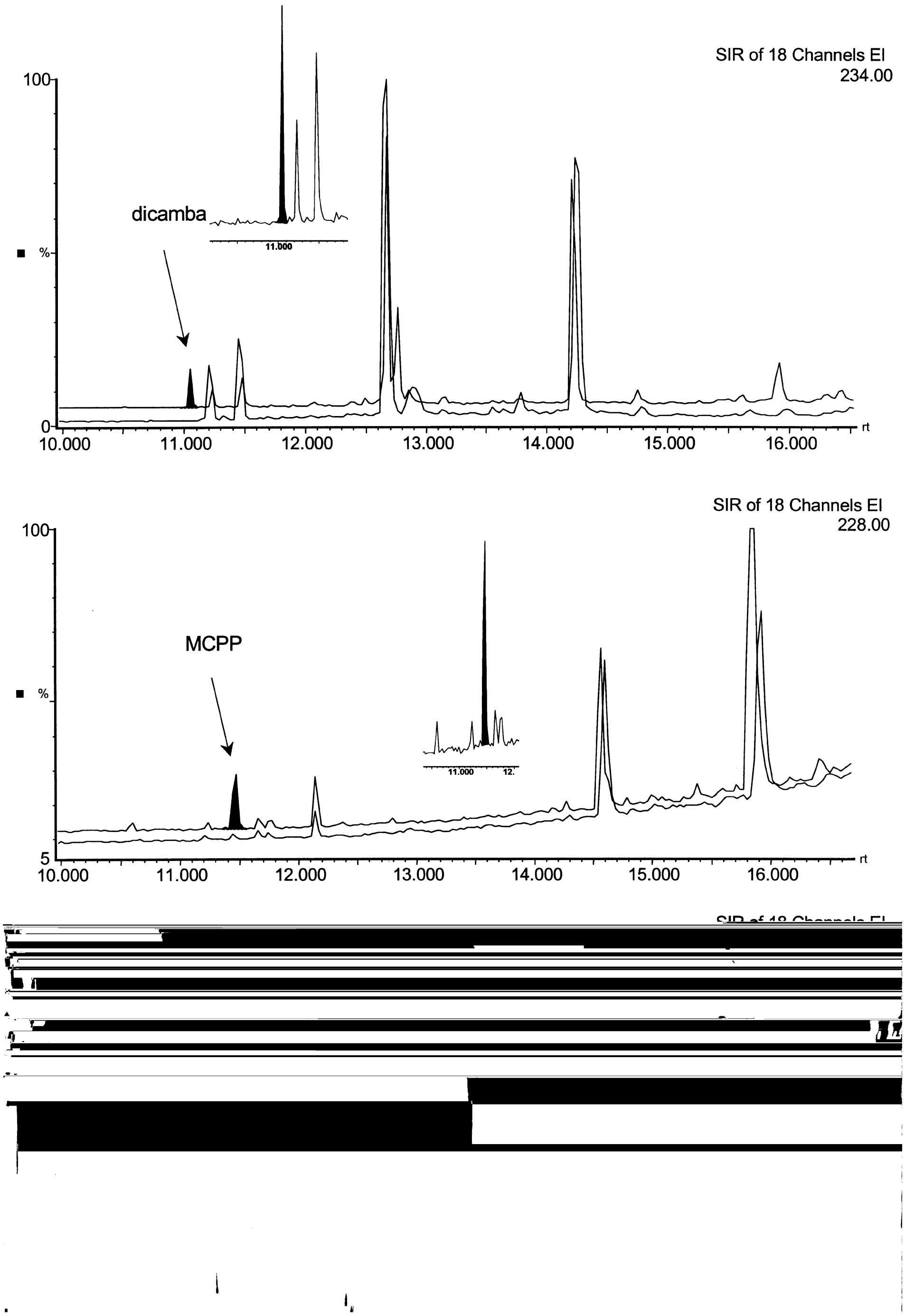


Fig. 10. LVI-GC–MS in the single ion recording mode of Rhine river water spiked with 0.3 μg/l each dicamba (234 m/z) and 2,4-DP (162 m/z), 0.5 μg/l each MCPP (228 m/z) and MCPA (214 m/z), 0.7 μg/l 2,4-DB (101 m/z), 0.9 μg/l MCPB (101 m/z), and 1 μg/l 2,4-D (199 m/z). Lower traces depict the non-spiked Rhine river water chromatogram. For details on miniaturised methylation-cum-extraction and 200-μl LVI, see text. 234, 228 and 214 m/z extracted, respectively, from the single ion recording chromatogram are depicted. rt=Retention time in min.

miniaturised approach, detection limits of 10-60 ng/l can be obtained with 800-μl samples.

The study illustrates that the role of ammonium salts as stabilisers of carboxylate anions, in conjunction with proper pH control, allows dimethyl sulphate to be used for the quantitative methylation of the phenoxy acids in water. Considering the instantaneous acidification of the matrix by the hydrolysis of DMS, this is a most gratifying result.

The possibility to extend this method to other groups of compounds, such as phenols and sulphonic acids, is being studied. In addition, less toxic derivatization reagents are being tested. Finally, the at-line coupling of the present fast sample preparation procedure with a similarly rapid separation–detection method, i.e., fast GC–time-of-flight MS will be attempted in the near future.

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