

Short Communication

Direct determination of metamitron in surface water by large sample volume injection

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ABSTRACT

For a number of applications, *e.g.*, monitoring of surface water quality, trace components which can be detected at levels of 0.1–1 ng do not need preconcentration. However, the determination of these components is usually performed after liquid–liquid or solid-phase extraction, which is time consuming. Injection of the sample directly into the separation system not only saves time (allowing higher sample throughputs), but is also uncomplicated and thus automatable. Metamitron was determined by direct injection of (surface) water samples onto an analytical C₁₈ column. With a 2-ml loop injection, the detection limit was 0.15 µg/l in surface water. No significant peak broadening compared with a 20-µl loop injection was observed. The linearity of the method was satisfactory ($r^2 = 0.9985$) and the relative standard deviation for seven replicate 2-ml injections at 2 µg/l was 3%. The total analysis time was only 10 min.

INTRODUCTION

So far, only a few low-level multicomponent methods [1–4] for surface water analysis have been reported. Especially for early warning systems these methods should be fast, reliable and capable of determining a broad range of relevant individual substances. The time available to decide whether the quality of a water is good enough, *e.g.*, for preparing drinking water, may not be more than 1–2 days after the first signal of an accidental discharge. For unknown components, this time is probably too short. Often the analyst tries to determine the component(s) by applying existing methods. Recoveries using, *e.g.*, extraction and/or derivatization are more or less unknown, so one can only determine the trend of a concentration profile rather than actual concentrations. In such events, an uncomplicated analytical method that does not involve any isolation or derivatization step is needed.

On June 14th, 1990, Dutch authorities were warned by the International Commission for Protection of the Rhine against Pollution (ICPR) about an accidental discharge (*ca.* 3 ton) of metamitron (4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one), an agricultural herbicide, at Leverkusen (Germany). Our existing

multicomponent methods were not applicable to this compound. Moreover, from literature it was known that the extraction efficiency using dichloromethane was poor and irregular [1-3]. Because the results obtained on a C_{18} concentration column [2] were good (85%), we decided to determine this component by direct injection of large volumes (2 ml) of surface water into an analytical C_{18} column, allowing simplicity and speed of analysis.

Data on large-volume injections are only sparingly available in the literature and usually refer to biological fluids [5-8]. The technique of direct concentration on the top of the column was more effective in reversed-phase compared to normal-phase chromatography [7], and data have been reported for injection volumes up to 2 ml. Direct aqueous injection has also been reported for the determination of N-methylcarbamates [9,10]. No loss of resolution was found and with large injection volumes detection limits at the ng/l level were expected.

In this paper we report our results obtained by direct injection, achieving a detection limit of 0.15 $\mu\text{g/l}$ (150 ng/l) with a total analysis time of *ca.* 10 min.

EXPERIMENTAL

Reagents

High-performance liquid chromatographic (HPLC) grade acetonitrile and water were obtained from Mallinckrodt (St. Louis, MO, U.S.A.) and perchloric acid from Baker (Deventer, The Netherlands).

Metamitron was obtained from Riedel-de Haën (Hannover, Germany).

Apparatus

For sample analysis the HPLC apparatus consisted of a Milton Roy (Riviera Beach, FL, U.S.A.) ConstaMetric 3000 pump to deliver the mobile phase and Pye Unicam Model 4110 and LC3 variable-wavelength UV absorbance detectors (Philips, Eindhoven, The Netherlands), set at 310 and 230 nm, respectively. For validation of the method the HPLC apparatus consisted of an LKB (Bromma, Sweden) Model 2150 pump and an LKB Model 2141 variable-wavelength UV absorbance detector.

Samples were injected using a Rheodyne injection valve with 0.02-, 0.1- and 2-ml loops. Chromatograms were recorded and integrated by a data station (Millipore, Bedford, MA, U.S.A.) using Baseline 810 software.

Procedures

Stock solutions of metamitron were freshly prepared each week by weighing followed by dissolution in acetonitrile. These solutions were diluted using HPLC-grade water to obtain standard solutions.

No pretreatment of surface water samples was performed except checking the pH, which should be between 6.5 and 7.5. The samples were separated on a reversed-phase column (LiChrospher 100 RP-18, 5 μm) (250 \times 4 mm I.D.) using acetonitrile-water (40:60, v/v) acidified to pH 2.7 with perchloric acid at a flow-rate of 1 ml/min.

RESULTS AND DISCUSSION

Chromatography

Metamitron can be detected at low concentrations using UV absorption at 230 or 310 nm, fluorescence or electrochemical [1] detection. The limit of detection is *ca.* 0.1–1 ng absolute [1,2]. On a C₁₈ column using acidified (perchloric acid) acetonitrile–water (40:60, v/v) mobile phase at pH 2.7 we found this component elutes with $k' = 2$.

With both UV detectors in series we first determined the response ratio (310/230 nm) for confirmation (identification); this value turned out to be 3.5. With loop injections of 0.02, 0.1 and 2 ml no significant band broadening in the system used (see Fig. 1) was observed.

From Table I, it can be seen that the peak width at half height ($w_{1/2}$) and at the peak base is the same for all volumes injected, indicating that metamitron is very efficiently concentrated from the aqueous sample on the top of the column. The increase in retention time from 4 to 6 min on going from 0.02 to 2 ml is in good agreement with the results of Broquaire and Guinebault [6], who reported a linear increase in retention time with the volume injected for components in non-eluting solvents.

From the results using 0.1- and 2-ml injections, the minimum detectable amount

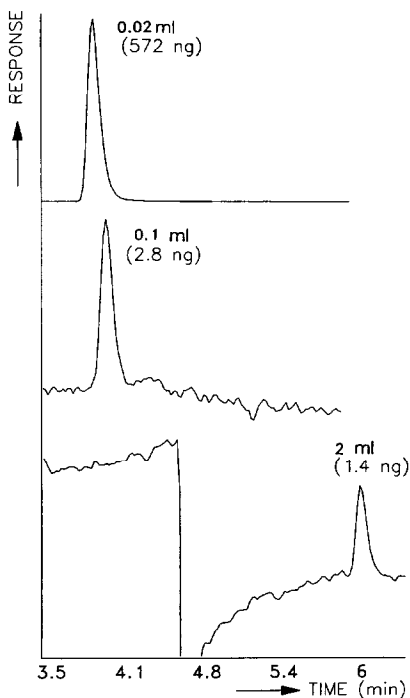


Fig. 1. HPLC of metamitron standard solutions using varying concentrations and loop volumes. Column, 250 × 4 mm I.D. LiChrosphere 100 RP-18, 5 μm; eluent, acetonitrile–water (40:60) at pH 2.7; flow-rate, 1.0 ml/min. UV detection at 310 nm.

TABLE I
DEPENDENCE OF RETENTION TIME AND PEAK WIDTH ON INJECTION VOLUME

Injection volume (ml)	Concentration ($\mu\text{g/l}$)	t_R (min)	Peak width (min)	
			$w_{\frac{1}{2}}$	Base
0.02	28600	3.92	0.11	0.21
0.1	28.6	4.03	0.12	0.19
2	0.7	6.05	0.17	

of metamitron was calculated to be *ca.* 0.3 ng, indicating that with large injection volumes of 2 ml no further concentration of the analyte of interest was necessary and that the detection limit (signal-to-noise ratio = 3) in surface water was *ca.* 0.15 $\mu\text{g/l}$.

The direct injection of 2-ml surface water samples showed that a wavelength of 310 nm was much more selective than 230 nm (see Fig. 2). From the inset in Fig. 2 it can also be seen that the response ratio (310/230 nm) at this low level (*ca.* 1.5 $\mu\text{g/l}$) may be used for confirmation (especially in the case when a warning has been issued against pollution by a particular compound, the concentration of which is far greater than that of all other unknown compounds in the water). Owing to the presence of dissolved organic constituents (DOC) in the surface water samples, metamitron is expected to be dragged along, resulting in a shorter retention time compared with a standard solution. This phenomenon was confirmed by comparing spiked with non-spiked surface water; the retention shift of metamitron was 32 s. From Table II it can be seen that the concentration profile in the river Rhine could easily be followed. Because this

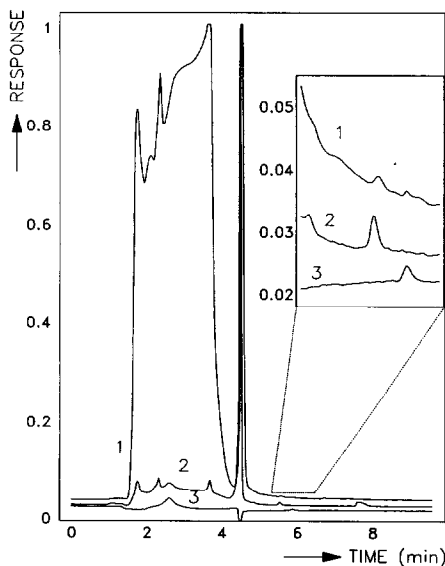


Fig. 2. HPLC of *ca.* 1.5 $\mu\text{g/l}$ metamitron samples using a 2-ml injection volume. (1) Surface water, detection at 230 nm; (2) surface water, detection at 310 nm; (3) standard, detection at 310 nm.

TABLE II

CONCENTRATIONS OF METAMITRON IN RHINE WATER AT LOBITH AFTER AN ACCIDENTAL SPILL

Sample data ^a	Time (h)	Concentration ($\mu\text{g/l}$)
17.06.90	06.00–12.00	0.4
	12.00–18.00	0.6
	18.00–24.00	0.9
18.06.90	00.00–06.00	1.4
	06.00–12.00	1.6
	12.00–18.00	1.3
	18.00–24.00	1.2
19.06.90	00.00–06.00	1.3
	06.00–12.00	0.7
	12.00–18.00	0.5
	18.00–24.00	0.4
20.06.90	00.00–06.00	<0.2
	08.10	<0.2

^a Composite or grab samples.

component is subject to EC regulation and the maximum admissible concentration (of any one pesticide) in drinking water is 100 ng/l, the intake of surface water for preparing drinking water was stopped for some time.

The validation of the method was determined using the LKB apparatus (see Experimental). The calibration graph (see Fig. 3) in the "real concentration" range (1–10 $\mu\text{g/l}$) was linear ($r^2 = 0.9985$). From the 95% confidence curve it can be seen that the limit of detection is 0.45 $\mu\text{g/l}$. Measurements using dual-wavelength detection, however, are much less sensitive than analyses at fixed wavelength owing to an increased noise level (more than a factor of ten according to the specifications). Two detectors in series might be the method of choice in trace analysis.

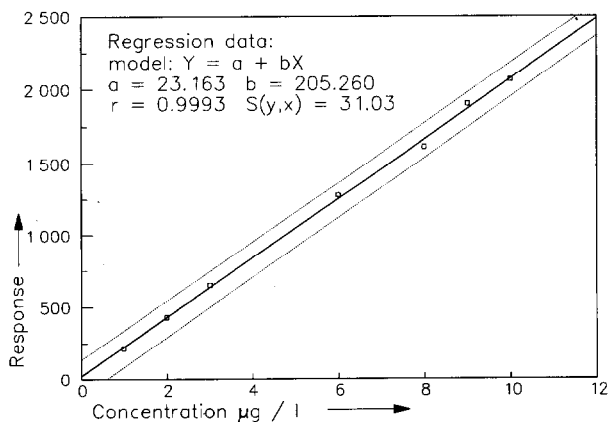


Fig. 3. Calibration graph with regression data and 95% confidence interval for metamitron. Injection volume, 2 ml.

The repeatability of 2-ml sample injections at 2 $\mu\text{g/l}$ was good (relative standard deviation 3%; $n = 7$). The mean recovery of spiked surface water at 2 $\mu\text{g/l}$ was 100.1%. More than 40 surface water injections of 2000 μl were applied to the analytical column without a significant decrease in performance. Neither clogging of the analytical column with particulate matter nor other adverse effects such as irreversible adsorption or memory effects were observed.

CONCLUSION

The determination of metamitron has been achieved by large-volume injections of samples of surface water directly into the analytical column. The limit of detection was 0.15 $\mu\text{g/l}$ using UV detection at 310 nm and applying 2 ml of aqueous sample to the column. The method is reliable and fast (*ca.* 10 min). The calibration graph showed a linear behaviour ($r^2 = 0.9985$) and the repeatability of 2-ml injections at 2 $\mu\text{g/l}$ showed a relative standard deviation of 3%.

The method is simple and indicates that components having sufficient retention on C_{18} columns and having good detectability can be determined very rapidly at low levels. This might be the preferred method if rapid decisions about water quality are necessary with regard to preparing drinking water.

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