Application Note No. 049

The Vision Automated Solid Phase Extraction System for GC-MS: An Evaluation of its Performance for Triazine Herbicides at ng/L Levels in Drinking Water

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Introduction

The UK drinking water regulations require that herbicides are analysed down to 0.1 μg/L (100 ng/L) levels and that detection limits of at least 0.02 μg/L (20 ng/L) are achieved. The percentage relative standard deviations (%RSD) for replicate samples should be better than 5%. It is customary that GC/MS in SIM mode is used for the separation and detection of the extracted analytes.

These requirements must be met by any new analytical procedure, however attractive it may otherwise be on a basis of economy or convenience. This application note details an evaluation of Vision, an automated solid phase extraction system, carried out in order to assess its suitability for the analysis of triazines in this context.

Instrumentation & Conditions

- **Vision:** Midas autosampler, Prospekt, solvent delivery unit and HPLC pump
- **Optic** 2-200 programmable injector
- **GC**: Shimadzu GC-17A with QP-5000 Mass Spectrometer in Selected Ion Monitoring mode
- **Column**: CP-Sil 5CB-MS 50 m x 0.25 mm i.d. x 0.4 μm film thickness
- **SPE Cartridge**: 10 mm x 2 mm i.d. containing 15-25μm styrene-divinyl benzene copolymer
- **Liner:** ATAS 'A' Type
- **Sample**: 7.5 mL tap water spiked with herbicide standards at 100 ng/l, 60 ng/l and 20 ng/l levels
- **Injection volume**: 50 μL

Extraction Method

- 10 ml spiked water samples were loaded into the Vision autosampler
- The SPE cartridge was activated and conditioned by flushing with acetonitrile and HPLC grade water
- 7.5 ml aliquots were sampled and the loop flushed with HPLC grade water
- The SPE cartridge was dried with helium
- The analytes were desorbed from the cartridge with ethyl acetate
- The whole eluent was injected into the GC-MS

Results

Please see the following pages for details of compounds analysed for, their relative standard deviations and the limits of detection using this method.

Conclusions

The 100 ng/l standard represents the reporting level for these compounds in drinking water. It can be seen from Results 1 that, in general, % RSDs are obtained in the range 1.32% - 4.82%, exceptions to this are des-isopropyl atrazine (7.23%) and ethyl parathion (15.33%). The relatively poor figure for ethyl parathion is believed to be due to an interfering ion.

With respect to detection limits, inspection of the results from the 20 ng/l standard show detection limits in the range 0.73 - 9.26 ng/l. These are well within the limit demanded, including ethyl parathion.

It should be noted that the sample was not pre-conditioned in any way.

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Results 1: Tap water spiked at 100 ng/L (SIM)

Ion (m/z)	Component	Peak Areas								Mean	Standard Deviation	% RSD	LOD (ng/L)*
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8				
158	Ethoprophos	106810	97496	92945	93367	93975	95782	92579	96519	96184	4648	4.83%	14.49
173	Des isopropyl atrazine	7144	6089	6325	6274	6416	7248	7161	7114	6721	486	7.23%	21.68
172	Des ethyl atrazine	102423	102714	100404	100757	101395	96846	97677	99498	100214	2109	2.10%	6.31
201	Simazine	35933	33856	33704	33523	33293	31658	32156	33129	33407	1276	3.82%	11.45
200	Atrazine	76781	73602	72667	73620	74691	71145	72686	73059	73531	1660	2.26%	6.77
214	Propazine	70573	69548	68577	70118	69203	66897	68256	68458	68954	1165	1.69%	5.06
214	Terbutylazine	101367	97325	96460	98765	97890	94660	96035	96707	97401	2021	2.07%	6.22
198	Metribuzine	65919	68382	67413	66461	65728	63909	63891	64822	65816	1599	2.43%	7.28
213	Desmetryn	93470	93706	92121	92760	92784	89335	91313	92045	92192	1392	1.51%	4.53
184	Prometryn	97828	104856	103354	105001	101272	101858	103370	103862	102675	2350	2.29%	6.86
185	Terbutryn	84574	84659	86878	84444	85461	83217	83739	84150	84640	1121	1.32%	3.97
225	Cyanazine	22144	22646	22263	22285	22033	20998	21165	21692	21903	575	2.62%	7.86
109	Ethyl parathion	32054	29317	24900	33742	22204	24539	24469	25025	27031	4143	15.33%	45.95

Results 2: Tap water spiked at 60 ng/L (SIM)

Ion (m/z)	Component	Peak Areas								Mean	Standard Deviation	% RSD	LOD (ng/L)*
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8				
158	Ethoprophos	69565	68022	65780	66927	61808	61227	62171	65752	65157	3096	4.75%	8.55
173	Des isopropyl atrazine	13221	12184	10885	10063	10427	10281	10138	11592	11099	1139	10.27%	18.47
172	Des ethyl atrazine	67377	64991	65756	65138	64712	63354	64702	65774	65226	1154	1.77%	3.18
201	Simazine	19722	17832	18954	18496	18906	18703	18285	19187	18761	577	3.07%	5.53
200	Atrazine	45882	44761	45889	44198	44877	44776	45551	44753	45086	614	1.36%	2.45
214	Propazine	41145	40609	40249	39560	39466	40899	40594	40433	40369	595	1.47%	2.65
214	Terbutylazine	64086	62465	62269	61498	60252	60045	60260	60950	61478	1400	2.28%	4.10
198	Metribuzine	40614	40563	40032	40333	40012	40104	40664	40977	40412	349	0.86%	1.55
213	Desmetryn	58545	57066	57392	57084	57041	56518	56995	57348	57249	587	1.03%	1.84
184	Prometryn	59701	60997	58907	62725	63339	64893	64326	61546	62054	2143	3.45%	6.21
185	Terbutryn	53043	52451	53568	51615	53186	53263	53627	54176	53116	785	1.48%	2.66
225	Cyanazine	14328	14547	13730	13277	12654	12754	12211	12371	13234	889	6.71%	12.08
109	Ethyl parathion	19844	21230	22905	17417	15884	16546	18360	19390	18947	2382	12.57%	22.61

*Limit of Detection (ng/L) = (n-1) x T factor (at 99% confidence level) x (standard deviation/mean peak area) x concentration (ng/L)

Results 3: Tap water spiked at 20 ng/L (SIM)

Peak Areas

Ion (m/z)	Component	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Mean	Standard Deviation	% RSD	LOD (ng/L)*
158	Ethoprophos	20665	20181	21156	18855	18197	19288	18867	19601	1084	**5.53%**	**3.48**
173	Des isopropyl atrazine	8087	6339	7287	6618	6667	7504	6624	7018	626	**8.92%**	**5.61**
172	Des ethyl atrazine	17353	19242	18590	18783	18077	17928	17622	18228	672	**3.69%**	**2.32**
201	Simazine	7618	7727	7299	7636	7439	7317	7237	7468	193	**2.58%**	**1.62**
200	Atrazine	15714	15725	15508	15425	14891	15669	15347	15468	294	**1.90%**	**1.19**
214	Propazine	17690	17507	17351	16337	16501	17467	16766	17088	542	**3.17%**	**1.99**
214	Terbutylazine	18260	18479	18484	18132	18061	18234	18004	18236	190	**1.04%**	**0.65**
198	Metribuzine	13079	13677	13590	13319	13396	14123	13799	13569	343	**2.53%**	**1.59**
213	Desmetryn	19458	19755	19498	19689	19374	19092	19311	19454	226	**1.16%**	**0.73**
184	Prometryn	20603	20296	20716	21045	20033	20521	20953	20595	355	**1.72%**	**1.08**
185	Terbutryn	17975	17903	18487	17985	18387	17987	18254	18140	233	**1.28%**	**0.81**
225	Cyanazine	7840	7675	8006	8228	8628	7332	8619	8047	482	**5.98%**	**3.76**
109	Ethyl parathion	5325	5671	7866	7029	7072	5785	7285	6576	968	**14.73%**	**9.26**

*Limit of Detection (ng/L) = (n-1) x T factor (at 99% confidence level) x (standard deviation/mean peak area) x concentration (ng/L)

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