

Determination of selected degradation products in w

SPE-GCMS high precision method

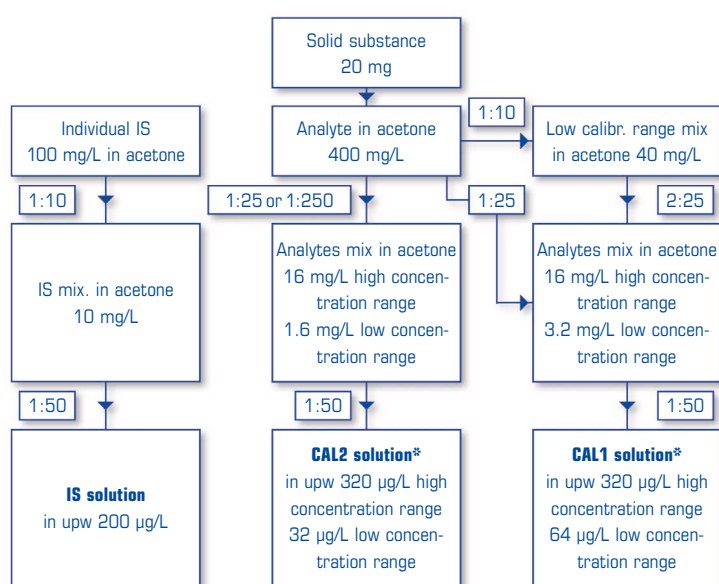


Figure 1: Flow chart for the preparation of the standard solutions

* Note: Last dilutions for CAL1 and CAL2 solutions were made daily

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EU regulations for pesticides in drinking water are the most restrictive in the world, allowing maximum concentrations (MCL) of 0.10 µg/L of any pesticide or of their degradation products in drinking water. Very accurate and precise method for the determination of the relevant compounds is therefore needed [1-12]. The standard method was modified using solid phase extraction (SPE) and gas chromatography – mass spectrometry [3-12], and the extended calibration through the overall

procedure with deuterated standard compounds [8-11]. At the target concentration level of 100 ng/L, the expanded uncertainty was approx. 10 %. The method proved very useful for target monitoring of selected herbicides, trend analysis and groundwater transport studies using low levels of herbicides as “natural tracers”.

Experimental – Materials

GCMS: GC-17A/QP-5050A with autosampler AOC-20i, Shimadzu, Japan. Silanized injection liners, SGE Australia. DB 5MS column, 30 m ID 0.25 mm, J&W, USA, Control. PC with CLASS 5000 software and NIST 21, NIST 107 and PMW TOX 2 spectral libraries.

One liter brown sampling bottles, Duran, Germany. Alltech SPE vacuum unit for 12 samples, USA. SPE cartridges EN 200 mg, Merck, Germany and Chromabond RP 200 mg, Macherey – Nagel, Germany. Gasses: helium, 99.9999 %; nitrogen 99.999 % purity, Messner, Slovenia. Acetone, methanol, ethylacetate, and dichloromethane (DCM) for GCMS analysis, Rathburn, Scotland. Hexachlorobenzene (HCB), solid, p.a., Fluka, Switzerland. Pure standard analytes and standard solutions of deuterated analytes, Dr Ehrenstorfer, Germany.

Methods – Preparations of standard solutions (Fig. 1)

Solid target analytes and standard solutions of deuterated analytes

were used. All spiking solutions were performed with serial dilutions in acetone.

SPE procedure (Fig. 2)

1.15 L of each sample, (standard (calibration) sample and control sample) were extracted using SPE cartridges at 3 – 5 mL/min. The cartridges were dried for 2 minutes and stored in the refrigerator at +4 °C (not longer than three days). The SPE cartridges were eluted with 10 mL of DCM. Traces of water were removed by anhydrous sodium sulphate. The eluate was dried with nitrogen and redissolved in 1 mL of 400 µg/L HCB solution in acetone or acetone/DCM.

GCMS analysis (Fig. 2)

1 µL of the solution was injected into the GCMS. A temperature programme from 50 °C (1 min.) to 270 °C with initial fast heating was used. The injector temperature was 280 °C and detector temperature 300 °C (METH2 in flow chart, Fig. 2). A daily control run was performed before each sample analysis (see Fig. 2). For S/N calculation, 1 µL of the HCB solution was injected in DCM, splitless mode.

The temperature programme from 80 to 220 °C with fast heating was applied. Scan range was between 40 and 350 and temperatures of the injector and detector were both maintained at 250 °C (METH1, Fig. 2). The same GCMS program (METH2, Fig. 2) and the same injection solvent were used for control run with

herbicides and their ater

endrin and p,p-DDT as well as for sample analysis.

Calculations

A calibration curve with area ratios (A/AIS) vs. mass ratios (m/mIS) was generated by linear regression within the limits of the calibration range. The calibration range was determined by statistical analysis of concentration data from real samples. For the extrapolation to LOD level and up from the upper calibration limit linear regression was not used, but response factor calculation, as described in EPA 525.2 and EPA 526.1. Extrapolation accuracy was checked with control samples.

Conclusions

For the determination of semi-volatile organic compounds, the SPE-GCMS method using internal standards is sufficiently accurate and precise.

For the best results for target monitoring it is important to select and adapt the calibration range according to each group of analytes. This can be achieved by using two calibration ranges, adapted to the expected concentrations of target compounds and MCL of 0.10 µg/L. The matrix selection for calibration, control and validation procedures is very important. For calibration and control sample natural spring water, free of any traces of target compounds was used, but with a similar organic matrix background. The statistical uncertainty budget was calculated ♦

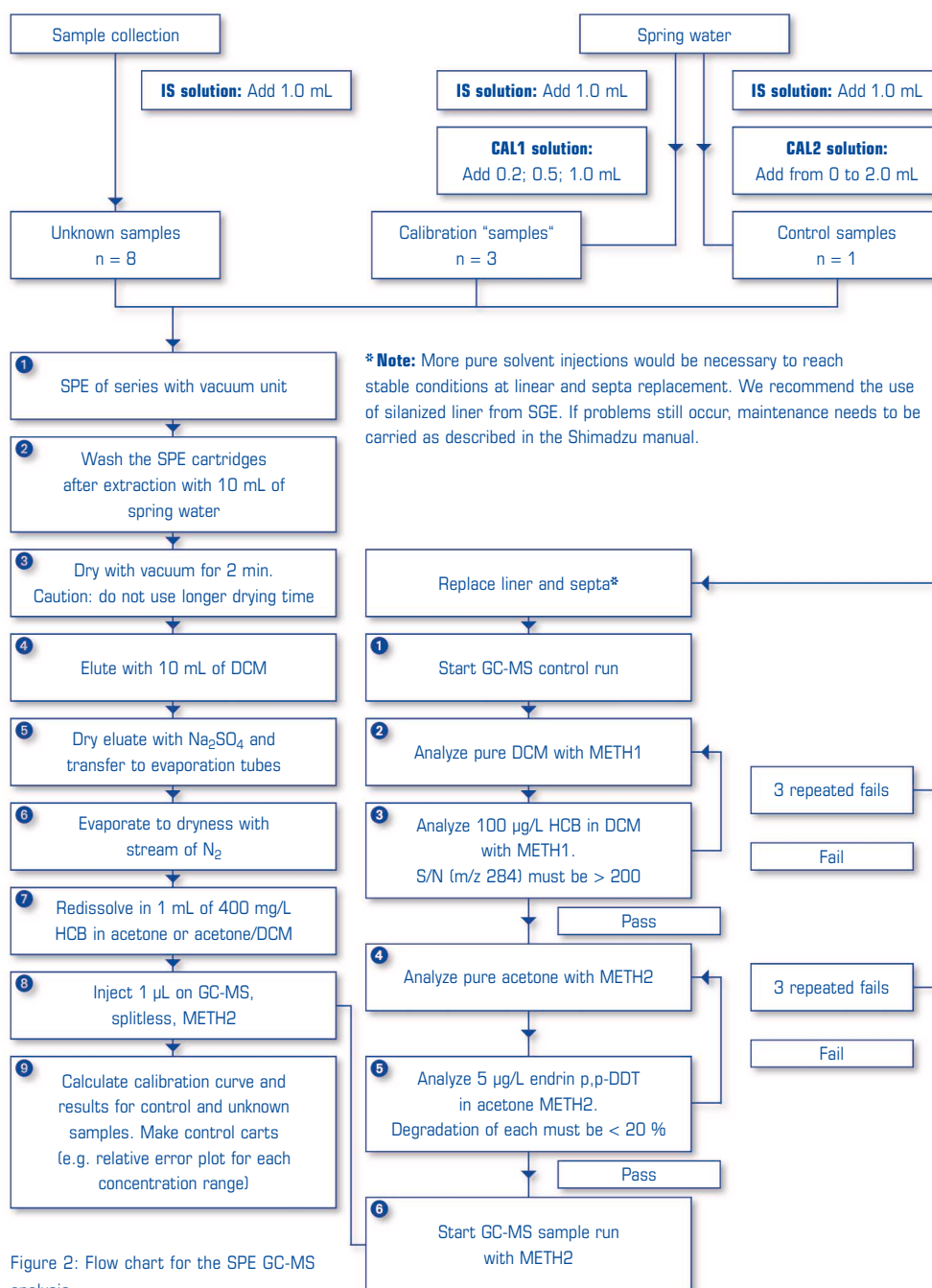


Figure 2: Flow chart for the SPE GC-MS analysis

Compound (CAS NO)	tr, min	SIM m/z (QVN / QVL1, QVL2)	LOD ng/L	LOQ ng/L	Working range ng/L
Desethylatrazine D6 – IS	12.09	175 / 173, 193	–	–	200
Desethylatrazine (6190-65-4)	12.16	175 / 173, 187	2.0	6.7	from 6.7 to 600
Desethylterbutylazine (30125-63-4)	12.47	186 / 145, 201	2.0	6.7	from 6.7 to 600
Hexachlorobenzene – CS	13.13	284 / 142, 249	–	–	400
Atrazine D5 – IS	13.66	205 / 178, 220	–	–	200
Atrazine (1912-24-9)	13.73	200 / 215, 173	2.0	6.7	from 6.7 to 600
Terbutylazine D5 – IS	14.16	219 / 234, 178	–	–	200
Terbutylazine (5915-41-3)	14.23	214 / 229, 173	1.0	3.3	from 3.3 to 600
Ametryn (834-12-8)	17.04	227 / 170, 212	5.0	16.7	from 16.7 to 600
Prometryn D5 – IS	17.08	247 / 232, 185	–	–	200
Terbutryn D5 – IS	17.65	246 / 175, 190	–	–	200
Terbutryn (886-50-0)	17.75	241 / 185, 226	5.0	16.7	from 16.7 to 600
Metolachlor D6 – IS	18.30	166 / 242, 246	–	–	200
Metolachlor (51218-45-2)	18.41	162 / 238, 240	2.0	6.7	from 6.7 to 600
Carbamazepin D10 – IS	28.62	203 / 246, 178	–	–	200
Carbamazepin (298-46-4)	28.81	193 / 236, 168	10.0	33.3	from 33.3 to 600

Table 1: Chromatographic characteristic and statistical parameters for target compounds in METH2, 1st SIM run

(LOD – limit of detection, LOQ – limit of quantification)

Compound (CAS NO)	tr, min	SIM m/z (QVN / QVL1, QVL2)	LOD ng/L	LOQ ng/L	Working range ng/L
3,4-dichloroaniline D2 – IS	9.12	165 / 163, 131	–	–	200
3,4-dichloroaniline (95-76-1)	9.33	161 / 163, 126	10.0	33.3	from 33.3 to 600
Desisopropylatrazine D5 – IS	11.90	178 / 160, 180	–	–	200
Desisopropylatrazine (1007-28-9)	11.92	158 / 173, 175	10.0	33.3	from 33.3 to 600
Desethylatrazine D6 – IS	12.08	175 / 173, 193	–	–	200
2,6-dichlorobenzamide (2008-58-4)	12.28	173 / 189, 175	2.0	6.7	from 6.7 to 600
Simazine D10 or D5 – IS	13.42	211 / 179, 193 or 206 / 174, 188	–	–	200
Simazine (122-34-9)	13.56	201 / 200, 186	2.0	6.7	from 6.7 to 600
Propazine D6 – IS	13.77	235 / 193, 220	–	–	200
Propazine (139-40-2)	13.83	214 / 229, 186	2.0	6.7	from 6.7 to 600
Prometryn D5 – IS	17.07	247 / 190, 232	–	–	200
Prometryn (7287-19-6)	17.16	241 / 184, 226	2.0	6.7	from 6.7 to 600

Table 2: Chromatographic characteristic and statistical parameters for target compounds in METH2 2nd SIM run.

Because of occasional interference of desisopropylatrazine 173 ion, ion 158 was selected

with GUM 1.2 modelling software [13].

At the concentration level of interest (100 ng/L), an expanded uncertainty of 10 % was determined. The procedure has been accredited according to ISO EN 17025 and inter-laboratory comparisons are consistently within the assigned range. Rigorous control of GCMS stability is still very important. Many additional procedures are described in EPA 525.2 and 526.1 methods and in equipment manufacture manuals. The use of internal standard method compensates the intra-day changes in GCMS stability and the calibration errors caused by the influence of the matrices.

Only a few deuterated standard compounds are available, which may be a disadvantage. Extreme care should be taken when a deuterated analyte is not available and daily use of control samples and rigorous validations are then necessary [14]. Many additional steps of validation procedures were described in the latest EU documents on pesticides analysis [2,15,16].

References

01. EURAU position paper EU1-01-A56, Keeping Raw Drinking Water Resources Safe from Pesticides, 2001.
02. Quality control procedures for pesticide residues analysis, Guidelines for Residues Monitoring in the

European Union, Third Edition 2003 Document No. SANCO/10476/2003 2003-08-27, http://EU_AGC_guidelines_5_September_2003.pdf

03. Organic Compounds by Liquid- Solid Extraction and Capillary Column GC/Mass Spectrometry, Environmental Protection Agency method, method 525.2, Rev. 2.0.
04. Determination of Selected Semi-volatile Organic Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS), Environmental Protection Agency method 526.1, Rev. 1.0.
05. Shimadzu application note, SCA 280-004.
06. Macherey – Nagel application note, No: 155.

07. R. Soniassy, P. Sandra, C. Schlett, Water Analysis Organic Micropollutants, Hewlett Packard, 1994, pp 73 - 100.
08. Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group – Determination of Selected Herbicides Metabolites and Their Degradation Products in Water Using Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry, O-2132-99.
09. P. Auersperger, J. Kus, B. Gorenc, Spremljanje koncentracije atrazina v podtalnici, Slovenski kemijski dnevi 2000, Maribor, 2000, pp 377-382.
10. P. Auersperger, J. Kus, Herbicides and their degradation products in groundwater of Ljubljansko Polje, 7th International Symposium Advances in Analytical Separation Science, Pörtscach/Wörthersee, 2002. Book of abstracts, pp 62.
11. P. Auersperger, J. Kus, Spremljanje koncentracije 2,6-diklorobenzamida v podtalnici Ljubljanskega polja, Slovenski kemijski dnevi 2003, Maribor, 2003, CD-ROM pp 172.pdf, 1-6.
12. ASTM D4128-01.
13. Eurachem/Citac Guide to Quantifying Uncertainty in Analytical Measurement, second edition, 2000.
14. ISO 10843-2:2000.
15. EURACHEM/CITAC guide, Traceability in Chemical Measurement; A guide to achieving comparable results in chemical measurement, 2003.
16. EURACHEM/CITAC, W.A. Hardcastle, Expression of Uncertainty in Qualitative Testing, Approaches to the Problem, LGC, 2002.