INTERNATIONAL STANDARD

ISO 27108

First edition
2010-04-15

Water quality — Determination of selected plant treatment agents and biocide products — Method using solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS)

Qualité de l'eau — Détermination d'agents de traitement et de produits d'usine sélectionnés — Méthode utilisant une micro-extraction en phase solide (MEPS) suivie d'une chromatographie en phase gazeuse-spectrométrie de masse (CG-SM)

Reference number
ISO 27108:2010(E)

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 27108 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

In recent years, ground water contamination as well as surface water contamination by pesticides has become a matter of public concern. Identification and quantification of pesticides at trace level concentrations often require both high sensitive chromatographic equipment and effective enrichment steps. In the analysis of aqueous samples, sample preparation techniques including solid-phase extraction (SPE) are frequently the most time-consuming steps and in many cases can be effectively replaced by solid-phase microextraction (SPME).

When using this International Standard, it may be necessary in some cases to determine whether and to what extent particular problems could require the specification of additional marginal conditions.

Water quality — Determination of selected plant treatment agents and biocide products — Method using solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the determination of the dissolved amount of selected plant treatment agents and biocide products in drinking water, ground water and surface water by solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS). The limit of determination depends on the matrix, on the specific compound to be analysed and on the sensitivity of the mass spectrometer. For most plant treatment agents and biocides to which this International Standard applies, it is at least 0,05 µg/l. Validation data related to a concentration range between 0,05 µg/l and 0,3 µg/l have been demonstrated in an interlaboratory trial.

This method may be applicable to other compounds not explicitly covered by this International Standard or to other types of water. However, it is necessary to verify the applicability of this method for these special cases.

NOTE Determinations by this International Standard are performed on small sample amounts (e.g. sample volumes between 8 ml and 16 ml).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

3 Principle

Substances under investigation are extracted from the water sample by solid-phase microextraction (SPME) according to their equilibrium of distribution. The extraction is performed by a chemically modified fused-silica

fibre, the surface of which is coated with a suitable adsorbent polymer. During extraction, the fibre is immersed in the liquid sample. After completion of the extraction procedure, the fibre is drawn back into the needle, removed from the sample vial, and introduced directly into the GC injector. The analytes are transferred to the GC column by thermal desorption.

The analytes are separated, identified and quantified by means of capillary gas chromatography with mass spectrometric detection (GC-MS) using electron impact (EI) ionisation mode.

Table 1 — Plant treatment agents and biocide products determined by this method

Name	Molecular formula	CAS registry No.	Molar mass	Reference No. in example chromatograms of Figure		
			g/mol	A.1	A.2	A.3
Dichlobenil	$C_7H_3Cl_2N$	1194-65-6	172,0	1	1	1
Desethylatrazine	$C_6H_{10}ClN_5$	6190-65-4	187,6	2	2	3
Desethylterbutylazine	$C_7H_{12}ClN_5$	30125-63-4	201,7	3	3	2
Simazine	$C_7H_{12}ClN_5$	122-34-9	201,7	4	4	7
Atrazine	$C_8H_{14}ClN_5$	1912-24-9	215,7	6	5	5
Lindane	$C_6H_6Cl_6$	58-89-9	290,8	7	6	8
Terbutylazine	$C_9H_{16}ClN_5$	5915-41-3	229,7	8	7	6
Metribuzine	$C_8H_{14}N_4OS$	21087-64-9	214,3	9	8	14
Parathion-methyl	$C_8H_{10}NO_5PS$	298-00-0	263,2	10	9	11
Heptachlor	$C_{10}H_5Cl_7$	76-44-8	373,3	11	10	9
Terbutryn	$C_{10}H_{19}N_5S$	886-50-0	241,4	12	11	12
Aldrin	$C_{12}H_8Cl_6$	309-00-2	364,9	13	12	10
Metolachlor	$C_{15}H_{22}ClNO_2$	51218-45-2	283,8	14	13	13
Parathion-ethyl	$C_{10}H_{14}NO_5PS$	56-38-2	291,3	15	14	15
exo-Heptachlorepoxide	$C_{10}H_5Cl_7O$	1024-57-3	389,3	16	16	16
Pendimethalin	$C_{13}H_{19}N_3O_4$	40487-42-1	281,3	17	15	17
endo-Heptachlorepoxide	$C_{10}H_5Cl_7O$	28044-83-9	389,3	18	17	18
Triclosan	$C_{12}H_7Cl_3O_2$	3380-34-5	289,5	19	18	19
Dieldrin	$C_{12}H_8Cl_6O$	60-57-1	380,9	20	19	20
Carfentrazone-ethyl	$C_{15}H_{14}Cl_2F_3N_3O_3$	128639-02-1	412,2	21	20	21
Diflufenican	$C_{19}H_{11}F_5N_2O_2$	83164-33-4	394,3	22	21	22
Mefenpyr-diethyl	$C_{16}H_{18}Cl_2N_2O_4$	135590-91-9	373,2	23	22	23

4 Interferences

4.1 Interferences during sampling

To avoid interference, collect samples as specified in Clause 7, observing the instructions specified in ISO 5667-1 and ISO 5667-3.

4.2 Interferences during extraction procedure

Commercially available SPME fibres differ frequently in quality. Variations in the selectivity of the materials also frequently occur from batch to batch, thus possibly causing significant deviations in extraction yield. This does not basically impair their suitability, apart from a resulting higher detection limit of individual substances.

Inadequately conditioned fibres frequently result in lower extraction yields and poorly reproducible results; therefore precondition new fibres according to Clause 8. Also condition used fibres by performing the whole SPME process using at least two sampling vials containing only water (5.1) prior to starting with the first sample of a new sample sequence.

Sensitivity of fibres gradually decreases throughout a sequence of samples. Therefore regular measurements of the reference solution within the sample sequence (see 9.1) are recommended. The fibre is still usable if the method shows required sensitivity for substances under investigation.

Adding sodium chloride to the sample results in a clear improvement of the extraction yield for most substances listed in Table 1. The addition of common salt (near saturation) is therefore recommended. Some substances listed in Table 1 show a reverse effect, which in most cases is weaker. Salt additions of < 20 % of the saturation concentration (e.g. about 0,5 g of NaCl in an 8 ml water sample) cause a deterioration in reproducibility. It is important to keep to exactly the same salt additions for all samples of a calibration sequence and/or sample sequence.

Salt deposits may accumulate in the metal syringe needle of the fibre holder after extended use. Salt deposits always occur when the syringe needle of the fibre holder is immersed in the water sample during extraction. This may damage the fibres and the injector liner. Therefore adjust the immersion depth precisely, and, if necessary, rinse out the SPME syringe needle to dissolve any encrusted salt.

To ensure that the measurements are of high accuracy and precision, keep extraction time constant (e.g. 60 min) within a sample sequence for all samples. It is highly preferable to use an automatic sampler with an SPME option.

For automatic operation, preferably use sampling vials with a thin septum (e.g. 0,9 mm to 1,3 mm thickness) in order to avoid any mechanical problems when piercing the septum of the sample vial with the metal syringe needle.

NOTE This is of particular importance when using automatic sampler systems that move sample vials in a circle, because otherwise damage to the piercing metal syringe needle (including the exposed fibre) can occur during extraction.

Extraction of some of the substances listed in Table 1 using the procedure according to Clause 8 depends on the temperature. As a rule, somewhat higher extraction yields are obtained at lower temperatures. Maintain extraction temperature constant (e.g. 30 °C) within a sample sequence for all samples in order to obtain reproducible extraction yields.

4.3 Interferences during gas chromatography and mass spectrometry procedure

Interferences may be caused, e.g. by the injection system used or by inadequate separation of the analytes. Experienced operators, using the information given in the instrument manuals, may be able to minimise this type of interference. Regular checking of the chromatographic and spectrometric system is required to maintain adequate performance. Required system stability should be checked regularly by the use of a GC standard.

Ascertain the necessary penetration depth for the fibres for thermal desorption in the GC injector. The penetration depth corresponds to the hottest point of the injector and shall be kept constant during a measuring sequence.

5 Reagents

The reagents shall be free from impurities possibly interfering with the GC-MS analysis.

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents, use, as far as available, “residual grade” or better in order to obtain low blanks. Verify by blank determinations and, if necessary, apply additional cleaning steps.

5.1 Water, complying with the requirements of ISO 3696, grade 1 or equivalent.

5.2 Operating gases for the gas chromatograph-mass spectrometer, of high purity and in accordance with manufacturer's specifications.

5.3 Sodium chloride, NaCl.

5.4 Solvents, e.g. ethyl acetate, $C_4H_8O_2$; acetone (propanone), C_3H_6O; acetonitrile, CH_3CN.

For the preparation of stock solutions of individual reference substances (5.9.2) use the appropriate solvent. However, it is recommended to prepare multi-component stock solutions (5.9.3) using either acetone or ethyl acetate.

5.5 Sodium hydroxide solution, w(NaOH) = 25 % mass fraction.

5.6 Hydrochloric acid, w(HCl) = 25 % mass fraction or **sulfuric acid**, $w(H_2SO_4)$ = 12,5 % mass fraction.

5.7 Sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5\ H_2O$.

5.8 Internal standard, e.g. atrazine-d_5, lindane-d_6 or parathion-ethyl-d_{10}.

As internal standard, choose a substance with similar physicochemical properties (extraction behaviour, retention time) as the substance to be determined. The internal standard should not be present in the sample to be analysed. The choice of a substance may be difficult and it depends on the problem to be resolved; in any case, the suitability should be checked. It is highly recommended to use a deuterium-labelled or ^{13}C-enriched substance listed in Table 1 as an internal standard. It may be advantageous to use more than one internal standard.

Prepare stock solutions of individual internal standard substances in the same way as specified for individual reference substances (5.9.2).

5.9 Reference substances

5.9.1 General

Reference substances (listed in Table 1) of defined concentration suitable for both the preparation of stock solutions and the preparation of spiked aqueous multi-component reference solutions used for calibration of the total procedure (9.2).

5.9.2 Stock solutions of individual reference substances

As an example, place 50 mg of a reference substance into a 100 ml one-mark volumetric flask (6.6), dissolve in an appropriate solvent (5.4) and make up to the mark with the same solvent.

Store stock solutions at temperatures between 1 °C and 5 °C according to ISO 5667-3, protected from light. They are stable for at least 12 months.

NOTE Deep freezing of stock solutions is also possible and commonly applied.

5.9.3 Multi-component stock solutions of reference substances

As an example, transfer 1 ml of each of the solutions of the individual substances (5.9.2) and the internal standard substances (5.8) into a 100 ml one-mark volumetric flask (6.6) and make up to the mark with ethyl acetate or acetone (5.4).

Store multi-component stock solutions at temperatures between 1 °C and 5 °C, protected from light. They are stable for at least 6 months.

5.9.4 Aqueous multi-component reference solutions used for calibration of the total procedure

Prepare the aqueous reference solution for calibration of the total procedure as follows.

Measure 100 ml of water, e.g. in a one-mark volumetric flask (6.6) and add a magnetic stir bar.

Place the flask on a magnetic stirrer and switch on.

Using a microlitre syringe, measure 10 µl of the multi-component stock solution (5.9.3) and dispense it below the surface of the stirred water. Continue to stir for about 5 min with the volumetric flask covered.

Adjust the agitation speed so that no turbulence funnel is formed.

Prepare reference solutions of higher and lower concentrations in the same way using correspondingly prepared multi-component stock solutions (5.9.3). All aqueous reference solutions suitable for multipoint calibration should contain equal amounts of internal standard.

Do not dilute the spiked aqueous solutions.

Always keep the spike volume constant.

NOTE A small spiking volume (e.g. 10 µl in 100 ml water) is recommended to avoid any interference of the solvent within the fibre adsorption process of the analytes under investigation.

Store reference solutions at temperatures between 1 °C and 5 °C, protected from light. They may not be stable for more than a few days and therefore shall be prepared each working day.

6 Apparatus

Equipment or parts of it which are likely to come into contact with the water sample or its extract shall be free from residues causing interferences. The use of vessels made of glass, stainless steel or polytetrafluoroethylene (PTFE) is recommended.

Usual laboratory equipment and in particular the following.

6.1 Sample flasks, e.g. brown glass, flat bottomed, with glass- or PTFE-coated stoppers, e.g. 100 ml or 250 ml.

6.2 Glass sample bottles (head space vials), with caps (6.3), e.g. 10 ml or 20 ml.

6.3 Crimp caps, with PTFE-coated septa (e.g. magnetic caps with butyl/PTFE septa, 0,9 mm to 1,3 mm).

NOTE Commercially available head space vials usually have a flanged rim suitable for a 3 mm septum. A thinner septum (e.g. 0,9 mm to 1,1 mm) requires suitable vials with a thicker flanged rim. Alternatively, a perforated spacer ring (e.g. made of natural rubber or butyl, 1,3 mm thick) can be placed between septum and crimp cap.

6.4 Crimper and decapper (e.g. manual crimper and manual decapper, 20 mm).

6.5 Graduated measuring cylinders, capacity, e.g. 100 ml or 250 ml, ISO 4788[3] class A.

6.6 One-mark volumetric flasks, capacity, e.g. 10 ml, 25 ml, 50 ml and 100 ml, ISO 1042[2] class A.

6.7 Single volume pipettes, capacities between 1 ml and 50 ml, ISO 648[1] class A.

6.8 Microlitre syringes, e.g. capacities between 5 µl and 50 µl.

6.9 Magnetic stirrer, including PTFE-coated magnetic stir bar of suitable size.

6.10 Capillary gas chromatograph with mass spectrometric detector (GC-MS) using EI ionisation mode, gas supply in accordance with the respective manufacturer's instructions.

6.11 Non-discriminating GC injector, e.g. splitless mode of a split or splitless injection system or programmable temperature vaporiser (PTV).

6.12 Automatic sampler with SPME option, including SPME syringe and the necessary software.

6.13 SPME fibres, e.g. 10 mm medium polar polyacrylate-phases (PA coating: e.g. 85 µm) or bipolar polydimethylsiloxane/divinylbenzene phases (PDMS/DVB coating: e.g. 65 µm). Other fibres as mentioned above may be applicable as well. However, it is necessary to verify their sensitivity for the substances under investigation (see 9.1).

NOTE Polyacrylate phases (PA 85) have proved to be most sensitive for the substances listed in Table 1.

Preferably use 23-gauge needles (particularly in combination with a septumless GC inlet system). If using a septum type injection system, 24-gauge needles should be used to reduce septum coring.

6.14 Capillary columns, for gas chromatography (examples of chromatographs appear in Annex A). It is advantageous to use non-polar columns (e.g. low-bleed 5 %-phenylsiloxane column).

6.15 Borosilicate glass fibre filter, fibre diameter of 0,75 µm to 1,5 µm, with inorganic binding material.

6.16 Centrifuge, e.g. capable of reaching 2 000 r/min with appropriate centrifuge tubes.

6.17 pH meter, with electrodes.

7 Sampling and sample pretreatment

Collect samples as specified in ISO 5667-1 and ISO 5667-3.

For sampling, use thoroughly cleaned, flat bottomed glass flasks (6.1). Rinse flasks and caps with the water to be sampled.

Fill the bottles completely with the water to be examined.

Dechlorinate water samples containing chlorine by immediately adding sodium thiosulfate pentahydrate (5.7), resulting in a concentration of approximately 100 mg/l.

Treat and analyse the samples as soon as possible after sample collection as specified in ISO 5667-3. Store the samples at temperatures between 1 °C and 5 °C, protected from light.

8 Procedure

8.1 Sample preparation and extraction

Remove any suspended matter by, for example, filtration of the sample through a glass fibre filter (6.15) or centrifugation (6.16) to remove suspended matter.

NOTE Filtration or centrifugation of drinking water samples is not mandatory.

The pH value of the water sample only requires adjustment if it is below 6 ± 0,2 or above 8 ± 0,2. In this case, adjust to pH 7 ± 0,2 with hydrochloric acid (5.6), sulfuric acid (5.6) or sodium hydroxide solution (5.5).

Add the internal standard (5.8) dissolved in ethyl acetate or acetone (5.4) (e.g. by adding a 10 µl aliquot to a 100 ml sample volume as described in 5.9.4).

For example, measure exactly 8 ml (or 16 ml) of the water sample being examined and pour into a 10 ml (or 20 ml) head space vial (6.2). The measured volume shall be equal for both calibration and sample measurement.

Choose the sample volume so that there is a distance of 15 mm to 25 mm between the level of the liquid and the upper edge of the vial.

CAUTION — This is particularly important in automatic systems which rotate the sample vials, causing rotation of the metal syringe needle (including the exposed fibre) during extraction to avoid any mechanical problems (broken fibre or broken needle). Take note of the information given in 4.2, paragraph 6.

Add sodium chloride (5.3) near saturation point, i.e. 0,3 g per millilitre of sample volume (e.g. 2,4 g NaCl in 8 ml water) and dissolve. Avoid concentrations of NaCl higher than 0,35 g/ml. Close with a septum fitted crimp cap (6.3) using a crimper (6.4). Place the vials in sampling sequence on the automatic sampler with SPME option (6.13).

Use SPME fibres (6.13).

Condition new fibres by heating them up in the "bake-out" station of the SPME automatic sampler or in the injector of the GC. Refer to the manufacturer's instructions for appropriate fibre bake-out times. Proceed with at least two sampling vials containing only water (5.1) within a new sample sequence prior to starting with the first sample. Recalibration is needed when a new fibre is installed.

Adjust the extraction temperature to approximately 30 °C (see 4.2). Maintain extraction temperature constant within a sample sequence for all samples in order to obtain reproducible extraction yields.

Set the agitation speed to a maximum reproducible value (e.g. 250 min^{-1}). In systems using a magnetic stirrer, pierce the septum approx. 3 mm from the middle.

Extraction time should be set to 60 min.

NOTE An extraction time of 60 min produces acceptable sensitivity for all substances listed in Table 1. However, depending on sensitivity requirements, shorter extraction times are possible.

Desorb in the injector for 10 min at 280 °C.

8.2 Gas chromatograph

Check the required system stability regularly. Adjust and optimise instrument parameter settings in accordance with the respective manufacturer's instructions.

For separation, use appropriate capillary columns (6.14) and adjust chromatographic conditions for maximum selectivity (see Annex A for examples).

8.3 Identification of individual compounds by means of GC-MS

Identify the sample component by matching both retention times and relative intensities of the diagnostic ions (Table 2) of sample components and reference substances (5.9).