INTERNATIONAL STANDARD

ISO 11423-1

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Water quality — Determination of benzene and some derivatives —

Part 1:
Head-space gas chromatographic method

Qualité de l'eau — Détermination du benzène et de certains dérivés benzéniques —

Partie 1: Méthode par chromatographie en phase gazeuse de l'espace de tête

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Foreword

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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.

International Standard ISO 11423-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods*.

ISO 11423 consists of the following parts, under the general title *Water quality — Determination of benzene and some derivatives*:

— *Part 1: Head-space gas chromatographic method*

— *Part 2: Method using extraction and gas chromatography*

Annexes A, B, C and D of this part of ISO 11423 are for information only.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

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Introduction

This part of ISO 11423 describes a head-space method of sample treatment for the gas chromatographic determination of benzene and some of its derivatives in water.

For an extraction procedure followed by gas chromatography, see ISO 11423-2.

Which of these methods is applicable in a given case depends for instance on the type of sample to be analysed and the instruments available to the analyst. The method used is then described in the test report.

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Water quality — Determination of benzene and some derivatives —

Part 1:
Head-space gas chromatographic method

1 Scope

The method described is applicable to the determination of benzene, methylbenzene (toluene), dimethylbenzenes (xylenes) and ethylbenzene (abbreviated hereafter to BTX) in homogeneous samples of water and waste water in concentrations above 2 µg/l. In samples that are organically polluted, the limit of determination may, depending on the matrix of the sample, be higher. High concentrations may be determined by diluting the sample.

A number of further derivatives and nonpolar compounds with similar physical properties may also be determined by this method. The applicability of the method should be verified for the particular water sample.

2 Principle

A defined volume of unfiltered water sample is heated in a gas-tight septum-covered vial. After establishment of equilibrium between the gaseous and liquid phases, an aliquot of the gaseous phase is transferred to a gas chromatograph. Separation of benzene and its derivatives is carried out by injection on two capillary columns with stationary phases of different polarity (e.g. by simultaneous splitting) and determination using a suitable detector (for identification of compounds see 7.3).

3 Interferences

Loss of BTX may occur during sampling, transport storage and preparation of samples due to evaporation and stripping. Volatile organic compounds in the ambient air may contaminate water samples and water used for blank tests, leading to high limits of detection and high blank values, respectively.

To avoid errors due to sorption or desorption of constituents, samples should not come into contact with plastics materials.

Compared with the extraction procedure in ISO 11423-2, interferences due to suspended matter or emulsifiers are less frequent with head-space analysis. Solvents can modify the normal equilibrium with the gaseous phase. The presence of a second liquid phase prohibits the use of the head-space method.

Specific problems in the gas chromatographic system shall be handled according to the manufacturer's instruction.

The determination may be hindered by superposition of other hydrocarbons, for instance mineral oil constituents, which may also result in column overload.

If the results from the two different columns differ significantly, repeat the analysis with another separating phase or a specific detector.

4 Apparatus

Keep all precleaned bottles and vials in an upside-down position for 1 h at 150 °C in a ventilated drying oven before use. After this procedure, protect them from pollution, for instance by covering them with aluminium foil while they cool and closing them as soon as they are cool.

4.1 Conical-shoulder bottles, nominal capacity e.g. 250 ml, of non-actinic glass with tight stopper or PTFE- or aluminium-lined cap.

4.2 Magnetic stirrer with PTFE-coated bars.

4.3 Heating device (e.g. water bath).

4.4 Pipettes, capacity e.g. 1 ml, 2 ml, 5 ml, 10 ml, 25 ml and 50 ml, made of glass.

4.5 Gas washing-bottle attachment with ground glass cone and sintered disc.

4.6 Graduated flasks, capacity 100 ml, 250 ml and 1 000 ml.

4.7 Crimp-top sampling vials with PTFE or aluminium-coated septum and filler cap, suited to the automatic head-space dosing system used.

4.8 Automatic head-space dosing system with thermostatting facility or **heatable gas-tight injection syringe**, nominal capacity 2,5 ml or 5 ml.

The correct choice of the syringe is essential to minimize the injection error.

4.9 Crimp-top vials with PTFE septum and filler cap, capacity 10 ml, for the stock solutions.

4.10 Gas chromatograph with glass insert assembly and flame ionization detector (FID), supplied with gases as specified by the manufacturer.

4.11 Capillary columns for gas chromatography (see annex B).

NOTE — If alkanes with retention times identical with BTX are expected, the Kovacs indices are useful for the choice of the columns used.

4.12 Injection syringes, capacity 50 µl and 100 µl.

5 Reagents

Use only reagents of recognized analytical grade and only water complying with 5.1.

5.1 Water for dilutions and the reagent blank.

The BTX content of the water shall be as low as possible. In case of contamination, the water may be treated as follows:

Fill the water into conical-shoulder bottles (4.1), place a gas washing-bottle attachment (4.5) near the bottom of the bottle, heat the water to approximately 60 °C. Pass a stream of nitrogen (approximately 180 ml/min) through the water for 1 h, then allow the water to cool to room temperature while still passing nitrogen through it. Close the bottle tightly and store in the dark.

If necessary, pass nitrogen through the water immediately before use.

Check the quality of the water before and after treatment. If contamination is still detected, use another gas for purification, or purify the gas used.

5.2 Operating gases for the gas chromatographic system (nitrogen, helium, hydrogen, synthetic air) according to the manufacturer's instruction.

5.3 Calibration standard substances, each of highest purity.

Benzene	C_6H_6
Methylbenzene (toluene)	C_7H_8
1,2-Dimethylbenzene (*o*-xylene)	C_8H_{10}
1,3-Dimethylbenzene (*m*-xylene)	C_8H_{10}
1,4-Dimethylbenzene (*p*-xylene)	C_8H_{10}
Ethylbenzene	C_8H_{10}

5.4 Dimethylformamide, $HCON(CH_3)_2$, as solution aid. Alternatively, **propan-2-one** (acetone), CH_3COCH_3, or **methanol**, CH_3OH, may be used.

Determine their reagent blanks as described in 7.3.

5.5 Potassium carbonate, K_2CO_3, anhydrous, kept for 2 to 3 days at 200 °C to remove adsorbed volatile organic substances, **or other salt.**

6 Sampling and sample preparation

Head-space analysis vials (4.7) may directly be used as sampling containers. If this is not possible, collect the samples in non-actinic glass conical-shoulder bottles (4.1). Use separate sets of containers for samples of waters with different levels of BTX content.

If necessary, e.g. to achieve a lower limit of detection or to alleviate matrix effects in polluted waters, add potassium carbonate (5.5) or another salt. Choose the quantity of potassium carbonate so that there is enough left at the chosen temperature to leave some undissolved residue. The ionic strength of this solution shifts the equilibrium distribution of BTX further towards the gas phase. To obtain constant conditions for head-space analysis, the quantities of salt added and the volumes of samples and blanks must be identical.

Potassium carbonate may be added during the sampling procedure, if head-space vials (4.7) are used directly. Place about 7 g to 8 g potassium carbonate per 5 ml of water sample into the vial and fill with the sample to the volume needed for analysis.

It may be preferable to take larger sample volumes, which are then divided and treated with potassium carbonate in the laboratory. The exact procedure shall be described in the test report.

When analysing gaseous waters, it is necessary to neutralize free carbon dioxide by addition of potassium carbonate to the head-space vials before performing the test. As the quantity added depends on the carbon dioxide content, the addition shall be done in such a way that the carbonate ion content in the vial is about 1 % mass fraction. If this procedure is used, the calibration shall also include this step.

If using conical-shoulder bottles (4.1), rinse them with the water to be sampled. Immerse the bottle horizontally into a surface water so that the bottle is filled without turbulence. If sampling from a tap, slowly fill the bottle to overflowing without turbulence.

Automatic samplers are only suitable if they are composed of glass and metals only, with as little possible plastics materials, and if they are not used under reduced pressure. Cool the sampling container to about 4 °C and use glass tube immersed in the sample container to convey the sample subquantities, to avoid losses.

Avoid taking composite samples, as there are always losses when mixing samples. It is possible to use the extraction procedure described in ISO 11423-2 and mix extracts, if only an average value is needed.

Parallel to taking the sample, take an air blank consisting of a head-space vial (4.7) filled with the air present at the sampling site, and a reagent blank using water (5.1).

If possible, start the analysis within 2 days after collection of the sample. If the sample has to be stored longer than 2 days, keep it in the conical-shoulder bottles. Store all samples at 4 °C in the dark.

Place an aliquot of the sample into a head-space vial (4.7) immediately after arrival of the samples in the laboratory, using dispensers or other equipment that does not require reduced pressure. Close the vial with the septum and the crimp cap and shake it, if appropriate, to partly dissolve the potassium carbonate.

Check the tightness of the crimp cap; if it can be turned, it can leak when heated.

7 Procedure

7.1 General

At the start of the procedure the laboratory shall establish whether the conditions chosen ensure a static equilibrium. A temperature of at least 60 °C for at least 1 h has been found sufficient. The minimum time and the temperature shall be the same for samples and blank. If the procedure is changed, repeat the check on the establishment of the equilibrium.

If using an automatic sample-dosing system (4.8) follow the manufacturer's instructions for optimization. Take care to avoid contamination of the system through samples.

After static equilibrium has been reached, inject an aliquot of the head space into the gas chromatograph, with calibration, handling blank and air blank samples arranged at the beginning and at the end of a sampling series.

If using manual sample-dosing, take an aliquot of the head space using the syringe (4.12) — heated to about 20 °C above the chosen temperature — to inject into the gas chromatograph. An injection volume of not more than 1 µl is recommended.

7.2 Gas chromatography

Adjust the gas chromatograph according to the manufacturer's instructions.

To ensure identification of the respective compounds, use at least two capillary columns with stationary phases of different polarity. It is advantageous to have both capillary columns mounted on one injector for simultaneous sample injection.

Glass or silica columns, coated with silicone or methyl silicone separating phases cross-linked (chemically bonded) with variable phenyl content may be used (see annex B).

For detection, use a flame ionization detector (FID) with linear operating characteristics over the measuring range. It may be necessary to use a more selective detector [e.g. mass spectrometer (MS), photo-ionization detector (PID)] to improve compound identification.

Use of two columns with stationary phases of different polarity does not completely exclude peak overlap. If the results from the two columns used differ, peak overlap may be the reason; in this case the lower value is usually more accurate than the higher one.

Example of gas chromatograms are given in annex C.

7.3 Blank measurement

Benzene is present ubiquitously in trace levels. For this reason, perform blank measurements using water (5.1) prior to and during a series of analyses. Blank measurements should include all steps of the analytical procedure from sampling to the evaluation of the gas chromatogram. If blank values are unusually high (more than 10 % of the lowest measured values), every step in the procedure shall be checked in order to find the reason for these high blank values. Blank values should be reduced as much as possible by various procedures such as elimination of contamination by ambient air and checking of the gas chromatographic or integration parameters.

If sample concentrations are close to the limit of detection, however, blank values higher than 10 % of the lowest measured value shall be tolerated.

The blank value shall be deducted only if the standard deviation of the blank value does not significantly exceed the standard deviation of the calibration function.

7.4 Identification of individual compounds

Identify an individual compound by comparing its retention time in the sample with that corresponding in the calibration solutions.

In order to ensure correct identification, the retention times should not differ from one another in a series of analyses by more than ± 0,02 min, given comparable concentrations, or ± 1 % of relative retention times under 2 min.

If there is no peak at the characteristic retention time using one column only, and the chromatogram is normal in all other respects, the substance is deemed not to be present.

If there is a peak at the characteristic retention time, the presence of the substance is possible, and the identity of the substance shall be confirmed by further analysis.

If there is also a peak at the characteristic retention time on a column with a different polarity, the presence of the substance is very probable. The confidence level of the determination is higher if the polarities of the columns are very different.

In highly polluted samples or samples with a complex matrix, the use of a third column may be necessary.

For a higher certainty, use another method of detection, e.g. PID or GC-MS[1)].

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1) When registering mass spectrometer signals with fixed mass adjustments, it should be noted that the identification of the molecular ion or main fragment ion alone is not enough for identification. It is necessary to use at least one other typical mass for identification. Using the complete spectrum is preferable.

If using GC-MS confirmation, the mass ratio of main ion to secondary ion should be within ± 10 % of the standard; if using PID, within 20 %.

In low-polluted waters, or waters whose matrix is well known before the analysis, identification is very probable using one column only, and quite certain using two.

The evaluation of the certainty of identification lies with the analyst and shall be described in conjunction with the results.

8 Calibration and adjustment

8.1 General

The calibration function obtained for a particular determinand is valid only for the concentration range and the sample pretreatment concerned, including the solvent used for preparing the calibration solutions. It is also dependent on the working condition of the chromatographic system, which has to be checked regularly.

For routine purposes an adjustment of the calibration function using the following procedure is necessary: take two calibration solutions, one in the range of 1 % to 20 % and the other at approximately 80 % of the linear working range, and analyse them twice. Determine the arithmetic mean at the two concentration levels, plot the concentration against the instrument response. Check this graph against the most recent calibration curve obtained by the full calibration procedure. If the graph falls within the confidence interval of the calibration curve, this curve may be retained, if not, perform a full calibration.

Table 1 explains the subscripts that are used in the following text.

Table 1 — Subscripts used in this part of ISO 11423

Subscript	Meaning
i	identity of the substance
e	value measured at calibration
t	total method
j	consecutive number for pairs of values

8.2 Calibration of the total method using an external standard

For calibration of the total method, use aqueous solutions of the compounds to be determined. Use dimethylformamide, propan-2-one or methanol (5.4) as solution aid, to ensure rapid and even distribution of the compounds in water. Choose the concentration of the solution aid so that the volume added is as small as possible (1 ml per litre of water as a maximum), so that there is no interference with the distribution equilibrium.

8.3 Preparation of the stock solution

Place into 10 ml crimp-top vials (4.9) 5 ml of dimethylformamide or other solvent (5.4) and 100 µl each of benzene and the other compounds needed. Close with the septum and shake vigorously. Prior to use, leave the solution at room temperature for 15 min.

Store the stock solutions preferably at – 20 °C in the dark; they are stable for at least a week.

8.4 Preparation of the calibration solution

Fill a graduated 1 000-ml-flask (4.6) with water (5.1) and place it on a magnetic stirring apparatus (4.2). Open the crimp-top vial (4.7) and take an appropriate amount of stock solution (usually 50 µl). Stir the water in the flask so that there is a vortex, and dose the stock solution into the water, dipping the tip of the syringe needle into the water.

Immediately after dosing the stock solution, reduce the rotational speed of the magnetic stirrer, close the flask and stir for another hour.

If 50 µl of stock solution are used, the concentration of benzene in this calibration solution is 878 µg/l.

Using a pipette, place 5 ml of this calibration solution into a head-space vial (4.7) containing potassium carbonate (5.5), if appropriate. Use separate pipettes for the different concentration levels.

Prepare calibration solutions with higher or lower concentrations in a similar way, reducing or increasing the amount of stock solution added. Table 2 shows examples of a series of calibration solutions.

Table 2 — Examples of calibration solutions

Measuring range mg/l	Amount of benzene in 5 ml stock solution µl	Amount of stock solution in 1 l water µl	Mass concentration in the calibration solution µg/l
1,0	50	100	878
0,6	20	100	351
0,2	10	100	176
0,1	50	10	87
0,06	20	10	35
0,02	10	10	18
0,01	10 µl in 10 ml solution aid	10	9

Further calibration solutions shall not be prepared by dilution of calibration solutions.

Prepare the calibration solutions immediately before use.

If several compounds are added to the solution aid, take into account the increase in volume: with six compounds added, for instance, the volume of the stock solution is increased from 5 ml to 5,6 ml. Calculate the mass concentration using the densities of the compounds given in table 3.

Table 3 — Densities of benzene and its derivatives

Compound	Density g/ml at 20 °C
Benzene	0,878
Methylbenzene	0,867
1,2-dimethylbenzene	0,881
1,3-dimethylbenzene	0,865
1,4-dimethylbenzene	0,861
Ethylbenzene	0,867

Prepare calibration solutions of concentrations not given in the table in a similar way, using 5 ml or 10 ml solution aid and appropriate amounts of stock solution.