German standard methods for the examination of water, waste water and sludge

Substance group analysis (Group F)

Determination of aniline derivatives by gas chromatography (F 16)

DIN 38407-16

ICS 13.060.50

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung – Gemeinsam erfaßbare Stoffgruppen (Gruppe F) – Teil 16: Bestimmung von Anilin-Derivaten mittels Gaschromatographie (F 16)

In keeping with current practice in standards published by the International Organization for Standardization (ISO), a comma has been used throughout as the decimal marker.

Foreword

This standard has been prepared by the Normenausschuß *Wasserwesen* (Water Practice Standards Committee) jointly with Study Group *Wasserchemie* (Water Chemistry) of the *Gesellschaft Deutscher Chemiker* (German Chemists' Society) (see Explanatory notes).

Expert assistance and specialized laboratories will be required to perform the analyses specified in this standard.

When using the standard, a check shall be made in each individual case as to whether and to what extent additional boundary conditions have to be specified.

Introduction

This standard describes a method of determining aniline derivatives by gas chromatography and nitrogen- or phosphorus-selective detection or mass-spectrometric detection after solid-liquid concentration or liquid-liquid extraction.

1 Scope

This standard specifies a method of determining the aniline derivatives, listed in table 1, which are present in ground water, surface water and drinking water in concentrations by mass exceeding 0,1 µg/l.

Whether the method is suitable for other compounds is to be established on a case-by-case basis.

Experiments have shown that, with this method, aniline itself can only be determined with accuracies of recovery between 20 % and 50 %. If the user, nevertheless, wishes to employ this method to determine aniline, the conditions set out in Appendix A should be observed for better results. In addition, the statistical parameters listed in table 4 shall be reported.

Interferences may occur if other types of water (e.g. rainwater, waste water) are analysed.

Table 1: Aniline derivatives for which the method has been tested

No.	Chemical name	Empirical formula	Molar mass, in g/mol	CAS[1]) number
1	4-bromoaniline	C_6H_6BrN	172,03	106-40-1
2	2-chloroaniline	C_6H_6ClN	127,57	95-51-2
3	3-chloroaniline	C_6H_6ClN	127,57	108-42-9
4	4-chloroaniline	C_6H_6ClN	127,57	106-47-8
5	3-chloro-4-fluoroaniline	C_6H_5ClFN	145,57	367-21-5
6	3-chloro-4-methylaniline	C_7H_8ClN	141,60	95-74-9
7	4-chloro-2-nitroaniline	$C_6H_5ClN_2O_2$	172,57	89-63-4
8	3,4-dichloroaniline	$C_6H_5Cl_2N$	162,02	95-76-1

(continued)

Continued on pages 2 to 10.

Translation by DIN-Sprachendienst.

In case of doubt, the German-language original should be consulted as the authoritative text.

Table 1 (concluded)

No.	Chemical name	Empirical formula	Molar mass, in g/mol	CAS[1]) number
9	3,3'-dichlorobenzidine	$C_{12}H_{10}Cl_2N_2$	253,13	91-94-1
10	2,6-diethylaniline	$C_{10}H_{15}N$	149,24	579-66-8
11	2,6-dimethylaniline	$C_8H_{11}N$	121,18	87-62-7
12	N,N-dimethylaniline	$C_8H_{11}N$	121,18	121-69-7
13	4-isopropylaniline	$C_9H_{13}N$	135,21	99-88-7
14	2-methyl-6-ethylaniline (6-ethyl-o-toluidine)	$C_9H_{13}N$	135,21	24549-06-2
15	2-methylaniline (o-toluidine)	C_7H_9N	107,16	95-53-4
16	2,4,5-trichloroaniline	$C_6H_4Cl_3N$	196,46	636-30-6
17	3-trifluoromethylaniline (3-amino-benzotrifluoride)	$C_7H_6F_3N$	161,13	98-16-8

[1]) CAS: Chemical Abstracts System.

2 Normative references

This standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the titles of the publications are listed below. For dated references, subsequent amendments to or revisions of any of these publications apply to this standard only when incorporated in it by amendment or revision. For undated references, the latest edition of the publication referred to applies.

DIN 12036 Narrow mouth, flat bottom flasks with conical ground glass socket and stopper, for laboratory use

DIN 12664-1 One-mark volumetric flasks with flanged rim, conical socket and conical joint, for laboratory use

DIN 12680-1 Graduated cylinders for laboratory use

DIN 12691 Class AS fast delivery one-mark bulb pipettes, with a waiting time of 15 seconds, for laboratory use

DIN 38402-12 German standard methods for the examination of water, waste water and sludge – General information (group A) – Sampling from stagnant waters (A 12)

DIN 38402-13 German standard methods for the examination of water, waste water and sludge – General information (group A) – Sampling from aquifers (A 13)

DIN 38402-14 German standard methods for the examination of water, waste water and sludge – General information (group A) – Sampling of untreated water and drinking water (A 14)

DIN 38402-15 German standard methods for the examination of water, waste water and sludge – General information (group A) – Sampling from flowing waters (A 15)

DIN 38402-51 German standard methods for the examination of water, waste water and sludge – General information (group A) – Calibration of analytical methods, evaluation of analytical results and linear calibration functions used to determine the performance characteristics of analytical methods (A 51)

DIN 38409-2 German standard methods for the examination of water, waste water and sludge – Parameters characterizing effects and substances (group H) – Determination of filterable matter and the residues on ignition (H 2)

3 Principle

After the pH of the sample has been adjusted to 9, the aniline derivatives are concentrated by means of solid-phase extraction using RP-C18 material or extraction with toluene, and then separated by gas chromatography using capillary columns, and quantified using a nitrogen- or phosphorus-selective detector or a mass-selective detector.

4 Interferences

4.1 Sampling

To avoid interference, the sample shall be collected as specified in clause 8, due attention being paid to the requirements given in DIN 38402-12 to DIN 38402-15.

4.2 Concentration by solid-phase extraction

Since commercially available RP-C18 material is often of varying composition and its quality and selectivity may fluctuate appreciably, even among batches supplied by the same manufacturer, only material from a single batch should be used for calibration and analysis.

The accuracies of recovery of individual compounds may vary as a function of their concentration and shall therefore be checked regularly at different concentrations and when a new batch is used.

If the sample contains suspended matter and precipitates which may block the packing, it shall be filtered through a glass fibre filter before concentration; this shall be indicated in the test report.

4.3 Gas chromatography

The presence of coextracted phenylurea herbicides in high concentrations may give rise to interference since the injection system used may cause them to undergo thermal decompositon to the corresponding aniline derivatives or isocyanates (cf. subclause 9.2).

5 Designation

Designation of the method of determining aniline derivatives by gas chromatography (F 16):

Method DIN 38407 – F 16

6 Apparatus

Preferably, glass, stainless steel or PTFE (polytetrafluoroethylene) equipment shall be used and those parts which come into contact with the sample or the extract shall be free of residues which can produce blank values.

The following equipment shall be used.

a) **Brown glass, narrow mouth, flat bottom flasks**, of nominal capacities 1 000 ml and 2 000 ml (e.g. DIN 12036 – E 1 000-G flat bottom flasks).

b) **Graduated cylinder**, of nominal capacity 1 000 ml (e.g. DIN 12680 – ME 1 000 graduated cylinder).

c) **Shaking funnel**, of nominal capacity 1 000 ml.

d) **6 ml polypropylene or glass cartridges**, filled with RP-C18 material.

e) **Vacuum or pressurized equipment**, for the concentration.

f) **Volumetric flasks or graduated glass vessels**, with inert closure, for collecting the eluates, and glass sample bottles (vials) with PTFE-coated septum for storing the eluate for autosampling.

g) **Volumetric flasks**, of nominal capacities 10 ml and 100 ml (e.g. DIN 12664 – MS A 10 volumetric flasks).

h) **Gas chromatograph**, for use with capillary columns, with nitrogen- or phosphorus-selective detector or mass-selective detector.

i) **Split and split-free injector**, direct injection system (on-column technique) or temperature-controlled injection system (cf. subclause 9.2).

j) **Capillary columns** (cf. Appendix B for examples).

k) **Borosilicate glass fibre filter**, with organic binder and a fibre diameter of 0,75 µm to 1,5 µm (cf. DIN 38409-2).

l) **pH meter**.

m) **Injection syringes**, of nominal capacity 5 µl or 10 µl.

n) **One-mark bulb pipettes**, of nominal capacities 10 ml, 20 ml and 50 ml (e.g. DIN 12691 – VPAS 10 pipettes).

7 Reagents

7.1 General

Only analytical grade reagents shall be used. The content of those impurities in the reagents and the water which contribute to the blank value shall be below the range of application of the method. The blank value shall be checked regularly and especially when a new batch is used.

The following reagents shall be used.

7.2 Gases, for gas chromatography and mass spectrometry, complying with the equipment manufacturer's instructions.

7.3 99,996 % (*V*/*V*) **nitrogen**, for drying and, if necessary, evaporating the eluates.

7.4 Sodium chloride, NaCl, roasted (e.g. by heating for one hour at 400 °C to 500 °C).

7.5 1 mol/l sodium hydroxide solution, NaOH.