SLOVENSKI STANDARD
oSIST ISO/DIS 17735:2018

01-september-2018

Zrak na delovnem mestu - Določevanje skupin izocianatov v zraku z reagentom 1-(9-antracenilmetil)piperazin (MAP) in tekočinsko kromatografijo

Workplace atmospheres - Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl)piperazine (MAP) reagent and liquid chromatography

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Air des lieux de travail - Dosage des groupements isocyanates totaux dans l'air par réaction avec la 1-(9-anthracénylméthyl)pipérazine (MAP) et par chromatographie en phase liquide

https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-9e86422d0882/sist-iso-17735-2019

Ta slovenski standard je istoveten z: **ISO/DIS 17735**

ICS:

13.040.30	Kakovost zraka na delovnem mestu	Workplace atmospheres

oSIST ISO/DIS 17735:2018 **en**

2003-01.Slovenski inštitut za standardizacijo. Razmnoževanje celote ali delov tega standarda ni dovoljeno.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-9e86422d0882/sist-iso-17735-2019

oSIST ISO/DIS 17735:2018

DRAFT INTERNATIONAL STANDARD

ISO/DIS 17735

ISO/TC **146**/SC **2**

Secretariat: **ANSI**

Voting begins on:
2018-02-15

Voting terminates on:
2018-05-10

Workplace atmospheres — Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl) piperazine (MAP) reagent and liquid chromatography

Air des lieux de travail — Dosage des groupements isocyanates totaux dans l'air par réaction avec la 1-(9-anthracénylméthyl)pipérazine (MAP) et par chromatographie en phase liquide

ICS: 13.040.30

iTeh STANDARD PREVIEW
(standards.iteh.ai)

SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-9e86422d0882/sist-iso-17735-2019

THIS DOCUMENT IS A DRAFT CIRCULATED FOR COMMENT AND APPROVAL. IT IS THEREFORE SUBJECT TO CHANGE AND MAY NOT BE REFERRED TO AS AN INTERNATIONAL STANDARD UNTIL PUBLISHED AS SUCH.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

This document is circulated as received from the committee secretariat.

Reference number
ISO/DIS 17735:2018(E)

© ISO 2018

oSIST ISO/DIS 17735:2018

iTeh STANDARD PREVIEW
(standards.iteh.ai)
SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-9e86422d0882/sist-iso-17735-2019

COPYRIGHT PROTECTED DOCUMENT

© ISO 2018

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Published in Switzerland

© ISO 2018 – All rights reserved

oSIST ISO/DIS 17735:2018

Contents

Page

iTeh STANDARD PREVIEW
(standards.iteh.ai)
SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-
SIST ISO 17735:2019

© ISO 2018 – All rights reserved

oSIST ISO/DIS 17735:2018

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 17735 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

iTeh STANDARD PREVIEW
(standards.iteh.ai)
SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-9e86422d0882/sist-iso-17735-2019

 © ISO 2018 – All rights reserved

oSIST ISO/DIS 17735:2018

Introduction

This International Standard specifies the use of 1-(9-anthracenylmethyl)piperazine (MAP) to measure monomeric and oligomeric isocyanate species in workplace atmospheres. MAP was designed to improve the reliability of identification of isocyanate species in sample chromatograms and to improve the accuracy of quantification of these species relative to established reagents. The high performance liquid chromatography (HPLC) analysis uses a pH gradient to selectively accelerate the elution of MAP derivatives of oligomeric isocyanates that might be unobservable in an isocratic analysis. The performance of MAP has been compared to other reagents used for total isocyanate analysis (Reference [7]). MAP has been found to react with phenyl isocyanate (used as a model isocyanate) as fast as or faster than other reagents commonly used for isocyanate analysis. The UV response of MAP derivatives is comparable to that of 9-(methylaminomethyl)anthracene (MAMA) derivatives and considerably greater than other commonly used reagents [approximately three times greater than 1-(2-methoxyphenyl)piperazine (1-2MP) derivatives of aromatic isocyanates and 14 times greater than 1-2MP derivatives of aliphatic isocyanates]. The compound-to-compound variability of UV response per isocyanate group for MAP derivatives is smaller than the variability of any other commonly used reagent/detector combination (the coefficient of variation is 3,5 % for five model isocyanates). This results in more accurate quantification of detectable non-monomeric isocyanate species based on a calibration curve generated from analysing standards of monomeric species. The monomeric species used for calibration is generally the one associated with the product being analysed, but others could be used due to the very small compound-to-compound response variability of the MAP derivatives. The intensity of fluorescence response of MAP derivatives is comparable to that of MAMA derivatives and considerably greater than other reagents (e.g. approximately 30 times more intense than that of tryptamine derivatives). The compound-to-compound variability in fluorescence response has been found to be smaller than that of MAMA derivatives but larger than that of tryptamine derivatives (MAMA = 59 % coefficient of variation, MAP = 33 % coefficient of variation, and tryptamine = 16 % coefficient of variation for 5 model isocyanates). The compound-to-compound fluorescence variability of MAP derivatives is considered too great for accurate quantification of non-monomeric isocyanate species based on calibration with monomer standards. However, the sensitivity of the fluorescence detection makes it especially suitable for quantification of low levels of monomer, and the selectivity is very useful to designate an unidentified HPLC peak as a MAP derivative. MAP derivatives also give a strong response by electrochemical detection. The pH gradient used in the HPLC analysis selectively accelerates the elution of amines (MAP derivatives are amines), and is very strong (it accelerates MDI more than 100-fold). Re-equilibration to initial conditions is almost immediate. Many oligomeric species can be measured in the 30 min MAP analysis that may be unobservable in a much longer isocratic analysis.

MAP has been used in several studies comparing it side-by-side with other methods. Reference [8] found MAP impingers and NIOSH 5521 impingers (comparable to MDHS 25) to give comparable results in spray painting environments. Reference [8] used MAP reagent, but the pH gradient was not employed. Reference [9] compared MAP impingers with several other impinger methods (NIOSH 5521 and NIOSH 5522) and the double filter method. The average MAP oligomer value was substantially higher than the other impinger methods and slightly higher than the double filter method. The pH gradient was used in these MAP analyses. Reference [10] found that the MAP oligomer results compared favorably against several other methods for measurement of oligomeric isocyanates in the collision repair industry, and agreed well with the reference values.

The MAP method is currently available as NIOSH Method 5525 (Reference [11]). The performance characteristics of the method have been evaluated in Reference [12].

© ISO 2018 – All rights reserved

iTeh STANDARD PREVIEW
(standards.iteh.ai)

SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f78-4de2-bb38-9e86422d0882/sist-iso-17735-2019

oSIST ISO/DIS 17735:2018

Workplace atmospheres — Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl)piperazine (MAP) reagent and liquid chromatography

1 Scope

1.01 This International Standard gives general guidance for the sampling and analysis of airborne organic isocyanates in workplace air.

1.02 This International Standard is appropriate for a wide range of organic compounds containing isocyanate groups, including monofunctional isocyanates (e.g. phenyl isocyanate), diisocyanate monomers (e.g. 1,6-hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI)), prepolymers (e.g. the biuret and isocyanurate of HDI), as well as chromatographable intermediate products formed during production or thermal breakdown of polyurethane.

iTeh STANDARD PREVIEW

1.03 In mixed systems of HDI and IPDI products, it is impossible to identify and quantify low levels of IPDI monomer using this International Standard, due to coelution of IPDI monomer with HDI-uretidinedione.

(standards.iteh.ai)

1.04 It is known that the method underestimates the oligomer in MDI-based products. Total isocyanate group (NCO) will be underestimated in MDI-based products by about 35% as compared to dibutylamine titration.

SIST ISO 17735:2019

1.05 The method has been successfully modified to be used with LC-MS-MS for TDI monomer using an isocratic 70% acetonitrile/30% 10 mM ammonium formate mobile phase.

1.06 The useful range of the method, expressed in moles of isocyanate group per species per sample, is approximately 1×10^{-10} to 2×10^{-7}. The instrumental detection limit for the monomers using both ultraviolet (UV) detection and fluorescent (FL) detection is about 2 ng monomer per sample. The useful limit of detection for the method using reagent impregnated filters is about 10-20 ng monomer per sample for both UV and FL detection. For a 15 l sample, this corresponds to 0.7-1.4 $\mu g.m^{-3}$. For impinger samples, which require solid phase extraction, experience has shown that the useful limit of detection is about 30-80 ng monomer per sample.

2 Normative references

2.01 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.

2.02 *ISO 5725-2, Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

2.03 *ISO 16200-1, Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography — Part 1: Pumped sampling method.*

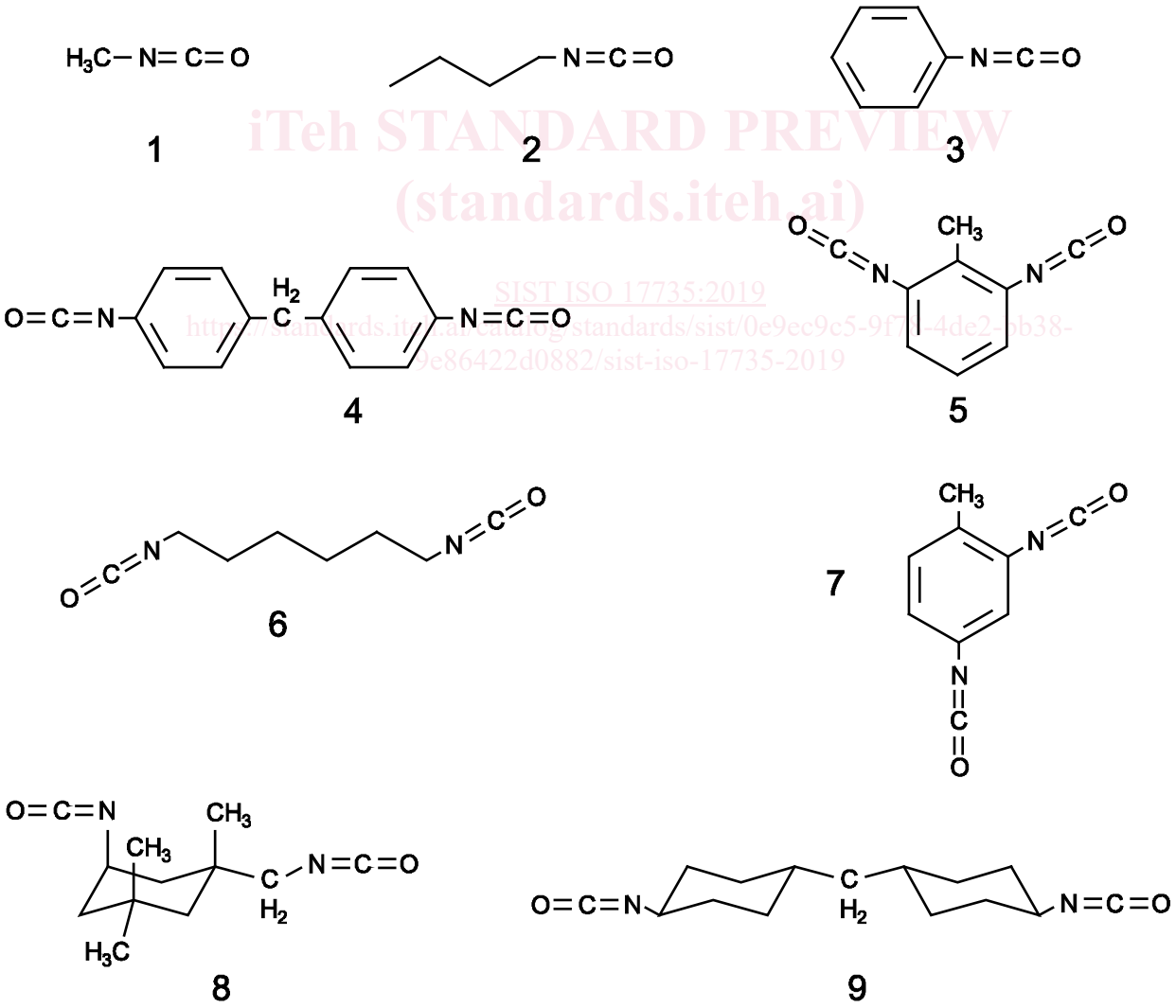
© ISO 2018 – All rights reserved

oSIST ISO/DIS 17735:2018

3 Principle

3.01 A measured volume of air is drawn through either an impinger containing a solution of 1-(9-anthracenylmethyl)piperazine (MAP), a filter impregnated with MAP, or a sampling train consisting of an impinger followed by an impregnated filter. The choice of sampler depends on the chemical and physical characteristics of the airborne isocyanate (Reference [13]). If an impinger is used, the solution is subjected to solid-phase extraction (SPE) and the eluate is concentrated and analysed by reverse phase high performance liquid chromatography (HPLC) with ultraviolet (UV) absorbance and fluorescence (FL) detection in series. If an impregnated filter is used for sampling, it is extracted with solvent either in the field after completion of sampling or in the laboratory. Waiting to extract the filter until after the sample has been received by the analytical laboratory is acceptable only for analysis of isocyanates collected as vapour. This solution is filtered and analysed by HPLC/UV/FL. Isocyanate-derived peaks are identified based on their UV and FL responses and by comparison with the chromatogram of a derivatised bulk isocyanate product if available. Quantification of compounds for which analytical standards are available (generally monomers) is achieved by comparison of the FL peak height of the sample peak with the FL peak height of standard matching solutions. Quantification of compounds for which analytical standards are not available is achieved by comparison of the UV area of the sample peak with the UV area of the appropriate monomer standard (i.e. the monomer from which the isocyanate product is derived).

3.02 Structures of some common diisocyanate monomers are shown in Figure 1.



iTeh STANDARD PREVIEW
(standards.iteh.ai)
SIST ISO 17735:2019
https://standards.iteh.ai/catalog/standards/sist/0e9ec9c5-9f7[illegible]-4de2-b38-9e86422d0882/sist-iso-17735-2019

Key

1 methyl isocyanate

2 butyl isocyanate

© ISO 2018 – All rights reserved

oSIST ISO/DIS 17735:2018

3 phenyl isocyanate
4 4,4'-MDI
5 2,6-TDI
6 HDI
7 2,4-TDI
8 IPDI
9 hydrogenated MDI (HMDI)

Figure 1 — Structures of some common isocyanates

4 Reagents and materials

4.01 CAUTION — Observe appropriate safety precautions when preparing reagents. Carry out preparations under a fume hood to avoid exposure to solvents, isocyanates or other volatile reagents. Wear nitrile gloves when manipulating reagents and solvents.

4.02 During the analysis, unless otherwise stated, use only reagents of HPLC grade or better, and water of HPLC grade. The following list of reagents are used for the below procedures and for the procedures in clauses 5 and 6: 9-(chloromethyl)anthracene, 1,6-hexamethylene diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), 4,4'-methylenebis(phenyl isocyanate), acetic anhydride, acetonitrile, butyl benzoate, dichloromethane, dimethyl formamide, ethyl acetate, formic acid, hexane, hydrochloric acid, isophorone diisocyanate, methanol, nitric acid, non-chromate/concentrated sulfuric acid-based cleaning solution, phosphoric acid, piperazine, prepurified nitrogen compressed gas, toluene, tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, and triethylamine.

4.03 The following materials are used for the below procedures and for the procedures in clauses 5 and 6: amber jars with polytetrafluoroethylene (PTFE)-lined caps, Büchner funnel, cool packs, cooler, disposable glass vials (7 ml and 20 ml, PTFE-lined caps), dropping funnel, filter holder (open- or closed-face 37 mm polystyrene cassettes, 13 mm polypropylene cassettes), filter paper, glass chromatography column (short), glass fibre filter (37 mm or 13 mm, binder-free), magnetic stirring bar, nylon filter (0,45 µm), round-bottomed flasks (250 ml two-necked; 100 ml one-necked; 1000 ml one-necked), separating funnel, silica gel (high-purity grade, 60 Å, 70-230 mesh), SPE tubes (normal phase silica gel, 6 ml/500 mg), syringe barrel (empty, polypropylene), syringe filter (0,45 µm PTFE), TLC plates (green fluorescing F_{254} or blue fluorescing F_{254s}), tubing (fluoroelastomer and plastic, rubber, or other suitable material 900 mm long), volumetric flask (10 ml one-mark, ISO 1042[1], class A), wax bath.

4.1 MAP reagent

4.1.01 MAP is prepared by the reaction of 9-(chloromethyl)anthracene with piperazine as shown in Figure 2.

4.1.02 The procedure is as follows.

4.1.03 Dissolve 10,8 mmol (2,47 g) of 9-(chloromethyl)anthracene (98 % mass fraction) in 25 ml dichloromethane. Place this solution in a dropping funnel.

4.1.04 Dissolve 54,4 mmol (4,69 g) of piperazine (99 % mass fraction) and 21,8 mmol (3,04 ml) of triethylamine (99,5 % mass fraction) in 37 ml dichloromethane. Place this solution in a 250 ml two-necked round-bottomed flask with a magnetic stirring bar.

4.1.05 While stirring this solution, add the 9-(chloromethyl)anthracene solution dropwise over a 30 min period. Rinse down the dropping funnel with an additional 10 ml of dichloromethane. Allow the reaction to continue while stirring for at least 2 h.

© ISO 2018 – All rights reserved

oSIST ISO/DIS 17735:2018

4.1.06 Using a separating funnel, wash the reaction mixture three times with 130 ml water by shaking vigorously for 1 min. Discard the emulsion that forms after the first wash, which contains primarily an impurity and not MAP. Discard the aqueous washings.

4.1.07 Place the washed MAP solution in a weighed 100 ml round-bottomed flask. Allow the dichloromethane to evaporate under a steady stream of nitrogen. Weigh the flask with the residue to obtain an approximate yield. This crude MAP can be safely stored in a freezer until further purification.

4.1.08 MAP is purified by column chromatography followed by sublimation. Using a glass chromatography column of internal diameter approximately 50 mm, add a slurry of silica gel (high-purity, 60 Å, 70-230 mesh) in toluene until the silica gel bed is approximately 80 mm deep. Wash the sides of the column down with toluene and allow the toluene to run through the column until the toluene is even with the silica gel surface.

4.1.09 Dissolve the crude MAP in 80 ml of toluene. Sonicate the mixture for 5 min and filter through filter paper. Save the filtrate. Suspend the residue in 20 ml toluene, sonicate for 5 min, and filter through filter paper. Discard the residue. Combine the filtrates and carefully load them onto the top of the silica gel bed. Pass an additional bed volume of toluene through the column. Discard the toluene eluate.

4.1.10 Begin to elute with ethyl acetate. Begin collecting 20 ml fractions in disposable vials with caps lined with polytetrafluoroethylene (PTFE). Monitor the fractions by spotting 1 µl of each on a thin layer chromatography (TLC) plate and viewing the intensity of the spots under UV light after the solvent has evaporated. This procedure indicates the presence of compounds in the fraction, which may or may not be MAP. Continue eluting with ethyl acetate until the yellow colour has eluted, which requires about 200 ml ethyl acetate. The MAP should be completely retained on the column at this point. After elution of the yellow colour, begin eluting with methanol, which requires 1 l – 1,5 l methanol.

4.1.11 The elution of the MAP can be readily followed by TLC. A portion of the fractions that had given a significant spot on the TLC plate are analysed by TLC (green fluorescing F_{254} or blue fluorescing F_{254s}, methanol) to determine which fractions contain MAP. Identify the MAP spot by comparing the retardation factor, R_f, of the aliquot spots with the R_f of a MAP standard.

4.1.12 Based on TLC analyses, combine the fractions containing pure MAP. Weigh a 1000 ml round-bottomed flask to be used for rotary evaporation. Add the combined fractions to the flask, but do not exceed half the volume of the flask at any given time. Heat the evaporator bath to 35 °C to 40 °C and use water aspirator vacuum. After evaporation and trace solvent removal from all of the combined MAP fractions under high vacuum, weigh the flask and its contents to assess the yield.

4.1.13 Purify the MAP powder further by sublimation. Dissolve the MAP in a small volume of dichloromethane (< 20 ml) and transfer the solution to a sublimation apparatus. Allow the dichloromethane to evaporate under a gentle stream of nitrogen, keeping the MAP below the level of the bottom of the coldfinger. When the dichloromethane has evaporated, seal the vessel and reduce the pressure with a vacuum pump to 6,67 Pa[1)] or less. Begin a slow flow of cold water through the coldfinger and place the sublimation vessel in a wax bath maintained at 125 °C to 130 °C. Sublimation takes many hours and may need to continue overnight. Sublimation is complete when there is no further growth of MAP crystals on the coldfinger and the small amount of material remaining at the bottom of the apparatus appears constant. When complete, remove the crystals from the coldfinger with a spatula. A typical yield is 2,2 g (74 % mass fraction). The melting point of the MAP is 146 °C to 147 °C. The purity of MAP as assessed by HPLC is typically 99 % mass fraction.

1) 1 Pa = 0,0075 torr.

© ISO 2018 – All rights reserved