BRITISH STANDARD

BS EN
13130-8:2004

Materials and articles in contact with foodstuffs — Plastics substances subject to limitation —

Part 8: Determination of isocyanates in plastics

The European Standard EN 13130-8:2004 has the status of a British Standard

ICS 67.250

NO COPYING WITHOUT BSI PERMISSION EXCEPT AS PERMITTED BY COPYRIGHT LAW

BSI
British Standards

National foreword

This British Standard is the official English language version of EN 13130-8:2004. It supersedes DD ENV 13130-8:1999 which is withdrawn.

The UK participation in its preparation was entrusted by Technical Committee CW/47, Materials and articles in contact with foodstuffs, to Subcommittee CW/47/1, Migration from plastics, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 17 June 2004

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 21 and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

© BSI 17 June 2004

ISBN 0 580 43969 0

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 13130-8

May 2004

ICS 67.250

English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 8: Determination of isocyanates in plastics

Matériaux et objets en contact avec les denrées alimentaires - Substances dans les matières plastiques soumises à des limitations - Partie 8 : Détermination des isocyanates dans les matières plastiques

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 8: Bestimmung von Isocyanaten in Kunststoffen

This European Standard was approved by CEN on 24 March 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

© 2004 CEN All rights of exploitation in any form and by any means reserved worldwide for CEN national Members.

Ref. No. EN 13130-8:2004: E

Contents

Foreword

This document (EN 13130-8:2004) has been prepared by Technical Committee CEN/TC 194 “Utensils in contact with food”, the secretariat of which is held by BSI.

This document was prepared by Subcommittee SC1 of TC 194 as one of a series of analytical test methods for plastics materials and articles in contact with foodstuffs.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2004, and conflicting national standards shall be withdrawn at the latest by November 2004.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

This standard is intended to support Directives 2002/72/EC [1], 89/109/EEC [2], 82/711/EEC [3] and its amendments 93/8/EEC [4] and 97/48/EC [5], and 85/572/EEC [6].

At the time of preparation and publication of this part of EN 13130 the European Union legislation relating to plastics materials and articles intended to come into contact with foodstuffs is incomplete. Further Directives and amendments to existing Directives are expected which could change the legislative requirements which this standard supports. It is therefore strongly recommended that users of this standard refer to the latest relevant published Directive(s) before commencement of a test or tests described in this standard.

EN 13130-8 should be read in conjunction with EN 13130-1

Further parts of EN 13130, under the general title *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation*, have been prepared, and others are in preparation, concerned with the determination of specific migration from plastics materials into foodstuffs and food simulants and the determination of specific monomers and additives in plastics. The other parts of EN 13130 are as follows.

Part 1*:* *Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants*

Part 2*:* *Determination of terephthalic acid in food simulants*

Part 3*:* *Determination of acrylonitrile in food and food simulants*

Part 4*:* *Determination of 1,3-butadiene in plastics*

Part 5*:* *Determination of vinylidene chloride in food simulants*

Part 6*:* *Determination of vinylidene chloride in plastics*

Part 7*:* *Determination of monoethylene glycol and diethylene glycol in food simulants*

Part 9*:* *Determination of acetic acid, vinyl ester in food simulants*

Part 10*:* *Determination of acrylamide in food simulants*

Part 11*:* *Determination of 11-aminoundecanoic acid in food simulants*

Part 12*:* *Determination of 1,3-benzenedimethanamine in food simulants*

Part 13*:* *Determination of 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) in food simulants*

Part 14*:* *Determination of 3,3-bis(3-methyl-4-hydroxyphenyl)-2-indoline in food simulants*

Part 15*: Determination of 1,3-butadiene in food simulants*

Part 16 *Determination of caprolactam and caprolactam salt in food simulants*

Part 17*: Determination of carbonyl chloride in plastics*

Part 18*: Determination of 1,2-dihydroxybenzene, 1,3- dihydroxybenzene, 1,4- dihydroxybenzene, 4,4'-dihydroxybenzophenone and 4,4'dihydroxybiphenyl in food simulants*

Part 19*: Determination of dimethylaminoethanol in food simulants*

Part 20*: Determination of epichlorohydrin in plastics*

Part 21*: Determination of ethylenediamine and hexamethylenediamine in food simulants*

Part 22*: Determination of ethylene oxide and propylene oxide in plastics*

Part 23*: Determination of formaldehyde and hexamethylenetetramine in food simulants*

Part 24*: Determination of maleic acid and maleic anhydride in food simulants*

Part 25*: Determination of 4-methyl-pentene in food simulants*

Part 26: *Determination of 1-octene and tetrahydrofuran in food simulants*

Part 27*: Determination of 2,4,6-triamino-1,3,5-triazine in food simulants*

Part 28*: Determination of 1,1,1-trimethylopropane in food simulants*

Parts 1 to 8 are European Standards.

Parts 9 to 28 are Technical Specifications, prepared within the Standards, Measurement and Testing project, MAT1-CT92-0006, "*Development of Methods of Analysis for Monomers*".

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

Isocyanates, characterised by the -NCO group, are monomers used for the manufacture of materials and articles intended to come in contact with food. During manufacture residual isocyanates can remain in the polymer and can migrate into food coming into contact with the polymer.

1 Scope

This part of this European Standard describes a method for the determination of individual and total levels of residual isocyanates in plastics materials and articles.

This method is applicable to the analysis of polyurethane polymers. The total level of isocyanate monomers in materials and articles determined according to the procedure described in this standard is given in milligrams of NCO per kilogram of material or article. The method is capable of quantitative determination of individual isocyanates measured as NCO at 0,04 mg/kg and total isocyanates at 1,0 mg/kg.

NOTE The method has been applied to the analysis of 9 isocyanate monomers listed in 3.1. It has not been applied to the analysis of octadecyl isocyanate, diphenylether-4,4'-diisocyanate or 3,3'-dimethyl-4,4'-diisocyanatobiphenyl as samples of these monomers have not been obtained. There is no reason to anticipate that the method may not be suitable for the analysis of these monomers also.

2 Normative references

This European 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 publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 13130-1:2004, *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 1: Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants.*

3 Principle

The procedure consists of two parts: screening and, if necessary, quantitative determination. Quantitative determination is applied only if isocyanates are detected by the screening procedure.

Materials and articles are initially screened for residual isocyanates by solvent extraction with dichloromethane and concurrent derivatization with 9-(methylaminomethyl)anthracene. 1-Naphthyl isocyanate is used during the screening procedure to check that the derivatization procedure has been successful. The resultant fluorescent derivatives are analysed by high performance liquid chromatography with fluorescence detection.

Materials found to contain residual isocyanates are quantified by standard addition to the material or article under test, using 1-naphthyl isocyanate as internal standard.

If interferences are experienced with the internal standard then calibration is carried out by standard addition omitting the internal standard, as described in annex A.

Confirmation of isocyanate levels is carried out by re-analysing the sample extracts on an HPLC column with different elution characteristics.

4 Reagents

WARNING: All chemicals are hazardous to health to a greater or lesser extent. It is beyond the scope of this standard to give instructions for the safe handling of all chemicals, that meet, in full, the legal obligations in all countries in which this standard may be followed. Therefore, specific warnings are

not given and users of this standard shall ensure that they meet all the necessary safety requirements in their own country.

NOTE 1 Isocyanates react extremely rapidly with moisture. Suitable precautions should be taken to ensure all glassware is dry. All laboratory glassware should be rinsed with diethyl ether (4.2.2) and baked at 105 °C overnight before use. After baking, vials should be placed in a desiccator and stored until required. Isocyanate standards should be protected from moisture and stored under refrigeration at -20 °C.

NOTE 2 All reagents should be of recognised analytical quality, unless otherwise specified.

4.1 Analytes

4.1.1 2,6-toluene diisocyanate $CH_3C_6H_3(NCO)_2$

4.1.2 diphenylmethane-4,4'-diisocyanate $OCNC_6H_4CH_2C_6H_4NCO$

4.1.3 2,4-toluene diisocyanate $CH_3C_6H_3(NCO)_2$

4.1.4 hexamethylene diisocyanate $OCNC_6H_{12}NCO$

4.1.5 cyclohexyl isocyanate $C_6H_{11}NCO$

4.1.6 1,5-naphthalene diisocyanate $C_{10}H_6(NCO)_2$

4.1.7 diphenylmethane-2,4'-diisocyanate $OCNC_6H_4CH_2C_6H_4NCO$

4.1.8 2,4-toluene diisocyanate dimer

4.1.9 phenyl isocyanate C_6H_5NCO

4.1.10 1-naphthyl isocyanate (internal standard, $C_{10}H_7NCO$), which contains no impurity at > 1 % by area which will elute at the same retention time as any of the nine individual isocyanate derivatives.

All standards should be of > 99 % purity.

4.2 Reagents

4.2.1 Dichloromethane (DCM, CH_2Cl_2), < 30 ppm H_2O, containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks. DCM should be dried over a bed of molecular sieve (5 Å) for 24 h prior to use.

4.2.2 Diethylether ($(C_2H_5)_2O$), at least 99 % purity.

4.2.3 9-(Methylaminomethyl)anthracene (MAMA, $CH_3NHCH_2C_{14}H_9$), containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks.

4.2.4 N,N'-Dimethylformamide ($HCON(CH_3)_2$), containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks.

4.2.5 Individual stock standard solutions (1000 µg/ml)

Weigh 0,01 g of isocyanate standard (4.1), to an accuracy of 0,1 mg, in a 10 l volumetric flask. Rapidly make-up to the mark with DCM (4.2.1) and shake thoroughly. Ultrasonification may be used as an aid to dissolution. Repeat the procedure to provide a second stock solution.

4.2.6 Individual intermediate standard solutions (100 ug/ml)

Put approximately 5 ml DCM (4.2.1) into a 10 ml volumetric flask. Using a 1000 µl syringe, dispense 1000 µl of stock solution (4.2.5) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly. Repeat the procedure using the second stock solution (4.2.5) to provide a second intermediate standard solution.

4.2.7 Individual dilute standard solutions (1 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 100 µl syringe, dispense 100 µl of intermediate standard solution (4.2.6) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

NOTE Individual dilute standard solutions should be prepared for each isocyanate (4.1).

4.2.8 Internal standard stock solution (1000 µg/ml)

Weigh 0,01 g of 1-naphthyl isocyanate (4.1.10), to an accuracy of 0,1 mg, into a 10 ml volumetric flask. Rapidly make-up to the mark with DCM (4.2.1) and shake thoroughly. Ultrasonification may be used as an aid to dissolution.

4.2.9 Intermediate internal standard solution (100 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 1000 µl syringe, dispense 1000 µl of internal standard stock solution (4.2.8) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

4.2.10 Dilute internal standard solution (1 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 100 µl syringe, dispense 100 µl of intermediate internal standard solution (4.2.9) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

NOTE Stock and standard solutions (4.2.5 to 4.2.10) should be stored with the exclusion of light and moisture at - 20 °C. They are stable for up to 1 month under these conditions.

4.2.11 Derivatization reagent solution (0,26 mg/ml)

Weigh 0,013 g of MAMA (4.2.3), to an accuracy of 0,1 mg, into a 50 ml volumetric flask. Make-up to the mark with DCM (4.2.1) and shake thoroughly.

NOTE Derivatization reagent should be prepared fresh daily, because of the photo-instability of MAMA, and stored with the exclusion of light.

4.2.12 Derivative dissolution solvent

Using a measuring cylinder, dispense 50 ml N,N'-dimethylformamide (4.2.4) into a 100 ml volumetric flask, make-up to the mark with the requisite HPLC mobile phase (7.1.5.1) and mix thoroughly.

4.2.13 Preparation of individual isocyanate derivatives for HPLC peak assignment

Using a 100 µl syringe, dispense 100 µl of dilute isocyanate standard solution (4.2.7) into a vial (5.4). Using a 1 ml syringe dispense 1 ml of derivatization reagent solution (4.2.11) into the same vial. Cap, gently agitate to mix the contents, and allow to stand for 60 min with the exclusion of light. Evaporate the vial contents to dryness under a stream of nitrogen, add 10 ml derivative dissolution solvent (4.2.12) and mix thoroughly. Ultrasonification may be used as an aid to dissolution.

Repeat for each isocyanate, using the individual dilute solutions (4.2.7).

NOTE Derivative solutions should be stored with the exclusion of light at ambient temperature. They are stable for up to two weeks under these conditions.

Repeat the procedure with the dilute internal standard solution (4.2.10).

5 Apparatus

5.1 General

An instrument or piece of apparatus is mentioned only if it is special, or made to particular specifications. Usual laboratory equipment is assumed to be available.

NOTE The MAMA-isocyanate derivatives are not sensitive to moisture and so glassware used for operations involving the derivatives need not be especially dried before use.

5.2 High performance liquid chromatograph, equipped with a fluorescence detector

Excitation Wavelength - 254 nm

Emission Wavelength - 412 nm

5.3 Chromatographic column

The column has to permit the separation of each of the MAMA derivatives of the nine individual isocyanates from one another as well as from that of the MAMA derivative of the internal standard. The peaks of the isocyanate standard derivatives and that of the internal standard derivative shall not overlap by more than 1 % of peak area with each other and with peaks resulting from other compounds.

The following are examples of HPLC columns found suitable for analysis of isocyanate derivatives:

a) 250 mm x 4,6 mm stainless steel column packed with silica, 5 μm particle size, 80 Å pore size,

220 m²/g surface area, octadecyl silyl bonded phase, 7 % carbon loading, partially end-capped;

b) 125 mm x 3,0 mm stainless steel columns packed as for a);

c) 250 mm x 4,6 mm stainless steel column packed with silica, 5 μm particle size, 120 Å pore size, 200 m²/g surface area, octadecyl silyl bonded phase, 11 % carbon loading, end-capped;

d) 250 mm x 4,0 mm stainless steel column packed as for c);

e) 125 mm x 4,0 mm stainless steel column packed with silica 5 μm particle size, 60 Å pore size, 220 m²/g surface area, octasilyl bonded phase, 11,5 % carbon loading, partially end-capped.

5.4 Glass vials

20 ml capacity with polytetrafluoroethylene-faced butyl rubber septa and aluminium crimp caps. Vials should be rinsed with diethyl ether (4.2.2), baked at 105 °C overnight and then stored in a desiccator until required for use.

NOTE Erlenmayer flasks, with a capacity of 25 ml, with ground glass joints can be used instead of 20 ml vials. They should be washed, dried and stored as for glass vials.

5.5 Glass sample vials suitable for the HPLC system employed.

5.6 Glass barrel syringes with needles, of 5 μl, 10 μl, 50 μl, 100 μl, 250 μl, 500 μl and 1000 μl capacities.

6 Samples

The laboratory samples of polymer materials or articles, to be analysed are obtained and stored as described in EN 13130-1.

The samples of plastics to be analysed have to be representative of the material, or article, presented for

analysis.

The following precautions are advisable:

a) to avoid cross contamination, carry out preparation of the polymer samples in an area remote to that used for handling isocyanate and MAMA solutions;

b) to avoid loss of isocyanates through hydrolysis, carry out preparation of the polymer samples in an area of low relative humidity and away from sources of moisture;

c) ensure that all glassware and syringes are dry before use.

7 Procedure

7.1 Test sample screening

7.1.1 Test sample extraction and derivatization

Using a representative sample, weigh 1 g, to an accuracy of 5 mg, of the test material or article into a vial (5.4), cutting into small pieces where possible. Add 10 ml of DCM (4.2.1) followed by 80 µl of dilute internal standard solution (4.2.10) and 1 ml of derivatizing reagent (4.2.11). Seal the vial and shake for 12 h on an orbital shaker. Using a Pasteur pipette, transfer the solvent extract to a clean dry vial and reduce in volume to about 5 ml under a gentle stream of nitrogen. Seal the vial and store at - 20 °C. Add a further 10 ml of DCM to the extracted test pieces, seal the vial and shake for a further 12 h on an orbital shaker. Remove the solvent extract and combine with the first extract. Evaporate the vial contents to dryness under a gentle stream of nitrogen. Add 10 ml of derivative dissolution solvent (4.2.12) and mix thoroughly. Ultrasonification may be used to aid dissolution. Filter through a 0,45 µm syringe filter (pre-purged with 2 ml HPLC mobile phase (7.1.5.1)) and transfer to an HPLC sample vial.

Prepare a second derivatized sample extract.

NOTE The MAMA derivatization reagent is photosensitive. The concurrent extraction/derivatization should be conducted with the exclusion of light.

7.1.2 Preparation of reagent blank sample

Prepare as in 7.1.1 but omit the addition of the polymer sample.

7.1.3 Preparation of internal standard check sample

Prepare as in 7.1.1 but omit the addition of the internal standard.

7.1.4 Preparation of un-derivatized sample blank

Prepare as in 7.1.1 but omit the addition of the derivatizing reagent and the internal standard.

7.1.5 Chromatographic determination

7.1.5.1 General

Depending on the type of chromatograph, column and detector used for the determination, the appropriate operational parameters should be established.

NOTE 1 The range of parameters which has been employed for the column a) (5.3) is as follows:

Mobile phase: Prepare a solution of 3 % triethylamine ($(C_2H_5)_3N$) (w/v) in water. Mix with acetonitrile to give 80/20 (v/v) acetonitrile (CH_3CN)/water. Adjust to pH 3,0 with orthophosphoric acid (H_3PO_4).

Flow rate	1 ml/min
Injection volume	20 µl
Temperature	ambient

Other conditions, which have been found to be suitable for the chromatographic separation of isocyanates, are as follows:

Column: d) (5.3)

Mobile phase A - 90/10 (v/v) water/acetonitrile (0,2 % tetrabutylammoniumhydrogen sulphate).

Mobile phase B - 10/90 (v/v) water/acetonitrile (0,2 % tetrabutylammoniumhydrogen sulphate).

Flow rate	1,5 ml/min.
Injection volume	10 µl

For advice on a suitable gradient profile see Figure C.1.

NOTE 2 If problems are experienced with stabilisation of retention times, the HPLC column can be operated in an oven or heating block at 40 °C.

7.1.5.2 Inject the individual isocyanate derivatives (4.2.13) to establish retention times of analytes and the internal standard derivative (4.2.13) under the chosen conditions.

NOTE 1 A typical chromatogram is shown in Figure B.1.

Inject the reagent blank sample (7.1.2), the internal standard check samples (7.1.3) and the un-derivatized sample blank (7.1.4) under the same chromatographic conditions.

NOTE 2 If peaks from the reagent blank sample (7.1.2) and the un-derivatized sample blank (7.1.4) co-elute with those of the isocyanate derivatives, the mobile phase should be adjusted to effect separation. Caution should be used when making adjustments as small changes, e.g.> 2 %, in composition can have a large effect on the elution time of some isocyanate derivatives. Separation can also be effected by using an alternative HPLC column.

7.1.5.3 Inject the derivatized sample extracts (7.1.1) and establish from retention times whether one or more of the isocyanate derivatives are present. The signal to noise ratio for the internal standard derivative has to exceed 3:1 as an indication that the derivatization and analysis has been successful.

If one or more isocyanate(s) is/are identified, it/they have to be quantified by the method of standard addition (7.2).

If isocyanate derivatives are identified in the sample and the internal standard check sample shows an interference at the retention time of the internal standard, isocyanates shall be quantified by standard addition, omitting the internal standard (see annex A).

NOTE If no isocyanate derivative peaks are detected at the expected retention times of the standard isocyanate derivatives and the derivatization has been shown to be successful then the test sample can be assumed to contain no individual isocyanate (as NCO) at > 0,04 mg/kg.

7.2 Quantification of isocyanates by standard addition

7.2.1 General

Where the presence of isocyanates is indicated by the screening procedure (7.1), quantification is carried out by standard addition.

7.2.2 Preparation of standard solutions for quantification (0 µg/ml to 5 µg/ml).

Into each of seven 10 ml volumetric flasks, dispense 0 µl, 5 µl, 10 µl, 50 µl, 100 µl, 250 µl and 500 µl of individual intermediate standard solution (4.2.6) of the isocyanate(s) identified (7.1.5.3). Make-up to the mark

with DCM (4.2.1) and mix thoroughly.

Prepare a second set of solutions using the second intermediate standard solution (4.2.6).

7.2.3 Procedure for standard addition

Using a representative sample, weigh exactly 1 g, to an accuracy of 5 mg, of the test material/article into each of seven vials (5.4), cutting into small pieces where possible. To each vial add 10 ml of DCM (4.2.1) followed by 500 µl of dilute internal standard solution (4.2.10), 1 ml of derivatizing reagent (4.2.11), plus 1 ml of each standard solution (7.2.2). Seal the vials and shake for 12 h on an orbital shaker with the exclusion of light. Using a Pasteur pipette, transfer the solvent extract to a clean dry vial and reduce in volume to about 5 ml under a gentle stream of nitrogen. Seal the vial and store at - 20 °C. Add a further 10 ml of DCM to the extracted test pieces, seal the vials and shake for a further 12 h on an orbital shaker. Remove the solvent extract and combine with the first extract. Evaporate the vial contents to dryness under a gentle stream of nitrogen. Add 10 ml of derivative dissolution solvent (4.2.12) and mix thoroughly. Ultrasonification may be used as an aid to dissolution. Filter through a 0,45 µm syringe filter, pre-purged with 2 ml HPLC mobile phase (7.1.5.1), transfer to a suitable sample vial.

Samples and standard addition solutions should be prepared in duplicate. The second set of samples and standard additions should be prepared using the second set of standard solutions (7.2.2).

NOTE Because quantification is by standard addition, it is important that the mass of sample taken for each standard addition point be kept constant.

7.2.4 Control sample

Prepare a control sample as in 7.1.1 but omit the addition of the polymer sample. Prepare a second control sample.

7.2.5 Analysis

Analyse standard addition samples and control samples (7.2.4) by HPLC, injecting each sample in duplicate. Identify the isocyanate derivatives and internal standard derivative peaks on the basis of their retention times and measure the respective peak areas.

NOTE Due to the non-uniform response of many commercially available fluorescence detectors, it may not be possible to obtain a linear response for all calibration solutions. If non-linearity is observed, the fluorescence detector should be optimised by decreasing the injection volume, or adjusting the slit-widths, so that the detector is linear over the desired range.

7.3 Evaluation of data

7.3.1 General

The following calculations assume that for all measurements exactly the same mass of test material/article has been used and that the same volume of dilute internal standard solution (4.2.10) has been added.

7.3.2 HPLC interferences

If the control samples (7.2.4) show any interference at the same retention time as the isocyanate derivatives the peak area of the interference shall be measured and quantified by constructing a standard addition curve, using the peak area ratio from the control sample in place of the zero-point of the test sample curve. Subtract the value for the un-derivatized sample from the value found for the derivatized sample.

8 Expression of results

8.1 Calculation by least squares regression

The two sets of calibrant solutions made from independently prepared stock solutions should be cross-checked by generating two standard addition curves which on the basis of peak area ratio measurement should agree to ± 5 % of one another.

For each isocyanate, calculate the isocyanate derivative/1-naphthyl isocyanate derivative peak area ratios obtained from the standard addition solutions and determine the gradient and intercept of the line using least squares regression.

If the regression line equation is:

$$y_{PAR} = bx + a \qquad (1)$$

where:

y_{PAR} is the peak area ratio of isocyanate derivative/1-naphthyl isocyanate derivative;

b is the slope;

a is the intercept.

Then the concentration of an individual isocyanate in the polymer is:

$$C_{iso} = a/b \qquad (2)$$

where:

C_{iso} is the concentration of an individual isocyanate, in milligrams of isocyanate per kilogram of polymer

a is the slope

b is the intercept

The concentrations of individual isocyanates should be converted to NCO equivalents by multiplication with the appropriate factor indicated below:

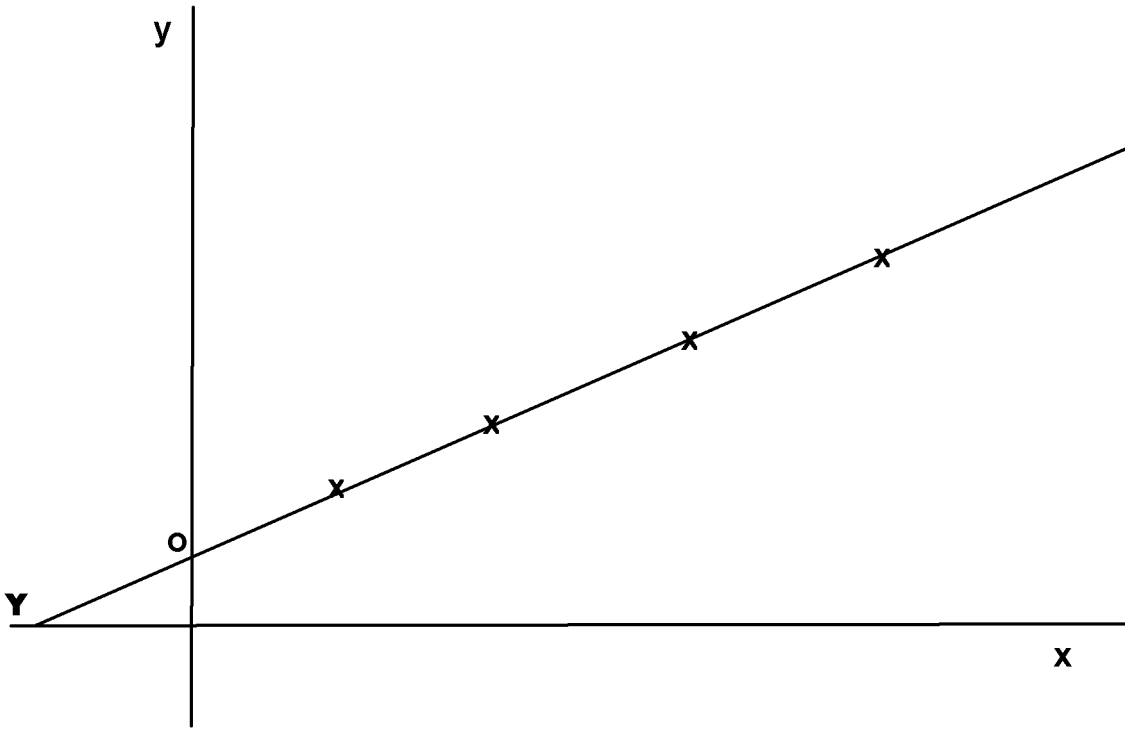
- 2,6-toluene diisocyanate	0,483
- diphenylmethane-4,4'-diisocyanate	0,336
- 2,4-toluene diisocyanate	0,483
- hexane diisocyanate	0,500
- cyclohexyl isocyanate	0,336
- 1,5-naphthalene diisocyanate	0,400
- phenyl isocyanate	0,353
- diphenylmethane-2,4'-diisocyanate	0,336
- 2,4-toluene diisocyanate dimer	0,483

Sum the values of NCO for each individual isocyanate to give the total NCO content.

This procedure yields directly the isocyanate concentration in the test sample in milligrams of isocyanate per kilogram of polymer.

8.2 Graphical determination using internal standard

Using the average value of the duplicate calibration values, construct a standard addition curve (see Figure 1) plotting isocyanate peak area/internal standard peak area (y axis) versus the isocyanate concentration added to the sample in milligrams per kilogram of polymer (x axis) .



where:

o is the peak area ratio resulting from the sample solution

x is the peak area ratio resulting from the fortified sample solutions

Figure 1 — Standard addition graph

Read the isocyanate concentration of the test sample by back extrapolation to the x-axis, where the magnitude of the intercept (Y) is equal to the isocyanate concentration.

Prepare a standard addition curve for each isocyanate identified.

The concentrations of individual isocyanates should be converted to NCO equivalents by multiplication with the appropriate factor indicated in 8.1.

Sum the values of NCO for each individual isocyanate to give the total NCO content.

This procedure yields directly the isocyanate concentration in the test sample, expressed in milligrams of NCO per kilogram of polymer.

8.3 Precision data and detection limit

8.3.1 General

Method performance has been evaluated by carrying out a precision experiment according to ISO 5725-1:1994 and ISO 5725-2:1994.

8.3.2 Repeatability

Evaluation of the results of the precision experiment at concentrations of 0,5 mg/kg and 1,0 mg/kg NCO for the 95 % probability level yielded the following performance characteristics:

The repeatability is as shown in Table 1.

Table 1 — Repeatability

Isocyanate	0,5 mg/kg	1,0 mg/kg
phenyl isocyanate	0,09	0,19
cyclohexyl isocyanate	0,07	0,13
2,4-toluene diisocyanate	0,09	0,10
2,6-toluene diisocyanate	0,08	0,10
1,5-naphthalene diisocyanate	0,09	0,10
diphenylmethane-2,4'-diisocyanate	0,11	0,14
diphenylmethane-4,4'-diisocyanate	0,07	0,13
hexamethylene diisocyanate	0,09	0,14
2,4-toluene diisocyanate dimer	0,07	0,13

8.3.3 Reproducibility

NOTE The reproducibility (R) values are being determined from collaborative trial results.

8.3.4 Detection limits

The within-laboratory detection limits (WDL), based on the calibration curve method according to DIN 32645, were as shown in Table 2.

Table 2 — Detection limits

Isocyanate (mg/kg)	Limit of detection
phenyl isocyanate	0,005
cyclohexyl isocyanate	0,006
2,4-toluene diisocyanate	0,009
2,6-toluene diisocyanate	0,010
1,5-naphthalene diisocyanate	0,003
diphenylmethane-2,4'-diisocyanate	0,009

diphenylmethane-4,4'-diisocyanate	0,006
hexamethylene diisocyanate	0,005
2,4-toluene diisocyanate dimer	0,031

Thus the method is capable of the detection of isocyanates, expressed as NCO, at 0,015 mg/kg.

9 Confirmation

9.1 Requirement for confirmation

In cases where total isocyanate levels in materials and articles exceed a restriction, e.g. QM (T) = 1 mg/kg in the final material or article (expressed as NCO), the determination has to be confirmed by the procedure in 9.2.

9.2 Confirmation by re-analysis on an HPLC column of different elution characteristics

Using an HPLC column with a different stationary phase, establish that the isocyanates determined to be present in the sample elute with different retention times than those seen in 7.1.5.3. The elution times of the isocyanate derivatives on the two columns should differ by more than ± 2 min.

Re-analyse the standard addition samples and the control samples. For each column, the peaks attributed to the derivatized isocyanate(s) should maximize within one-half peak width (H/2) or within 2 % of the absolute retention time of the fortified samples, whichever is the smaller. If the levels of putative isocyanates found using the two columns agree to within 10 %, then the average of the two values shall be considered to be the true value.

NOTE The individual isocyanate derivatives (4.2.13) should be used to establish the difference in elution times for the HPLC columns. If more than one isocyanate has been determined to be present in the sample (7.1.5.3) it can be necessary to reanalyse using two or more HPLC columns to ensure that the ± 2 min difference in elution times is met for each isocyanate derivative. Column packings which have been found to produce different elution times are as follows:

a) Silica, 5 μm particle size, 80 Å pore size, 220 m^2/g surface area, octadecylsilyl bonded phase, 7 % carbon loading, partially end-capped;

b) Silica, 5 μm particle size, 80 Å pore size, 220 m^2/g surface area, octadecylsilyl bonded phase, 12 % carbon loading, fully end-capped;

c) Silica, 5 μm particle size, 80 Å pore size, 220 m^2/g surface area, octylsilyl bonded phase, 6 % carbon loading, fully end-capped;

d) Silica, 10 μm particle size, 85 Å pore size, 350 m^2/g surface area, octadecylsilyl bonded phase, 5 % carbon loading, not end-capped;

e) Silica, 5 μm particle size, 70 Å pore size, 330 m^2/g surface area, octadecylsilyl bonded phase, 20 % carbon loading, fully end-capped.

10 Test report

The test report shall contain the following, where known:

a) a reference to this part of this standard;

b) all information necessary for complete identification of the sample;

c) form of the plastics;

d) use /class of food for which the sample is intended to contact, where known, and where possible food classification reference number as listed in Table 2 of EN 13130-1:2004;

e) intended conditions of use, where known;

f) any departures from the standard method, reasons for the departures;

g) any particular requirements of the parts of this standard;

h) any relevant comments on the test results;

i) details of any confirmation procedure(s);

j) limitation on the substance, that is 1 mg per kilogram of final product (expressed as NCO);

k) identity of the laboratory conducting the test and the name of the analyst;

l) date of sample arrival or sampling, the method of sampling, the date of the analysis, together with note on any intervening storage conditions;

m) individual test results, and the mean of two or more determinations satisfying the repeatability criterion of 8.3.1, expressed in milligrams of isocyanate per kilogram of polymer.

Annex A
(normative)

Calibration by standard addition omitting the internal standard

In cases where interferences are experienced with the internal standard, calibration is carried out using standard addition omitting the internal standard. In this instance, practically the same procedure as described in this standard should be followed but omitting the addition of the internal standard to the calibration and test samples. Evaluation of data, therefore, is analogous to the procedure described in clause 7

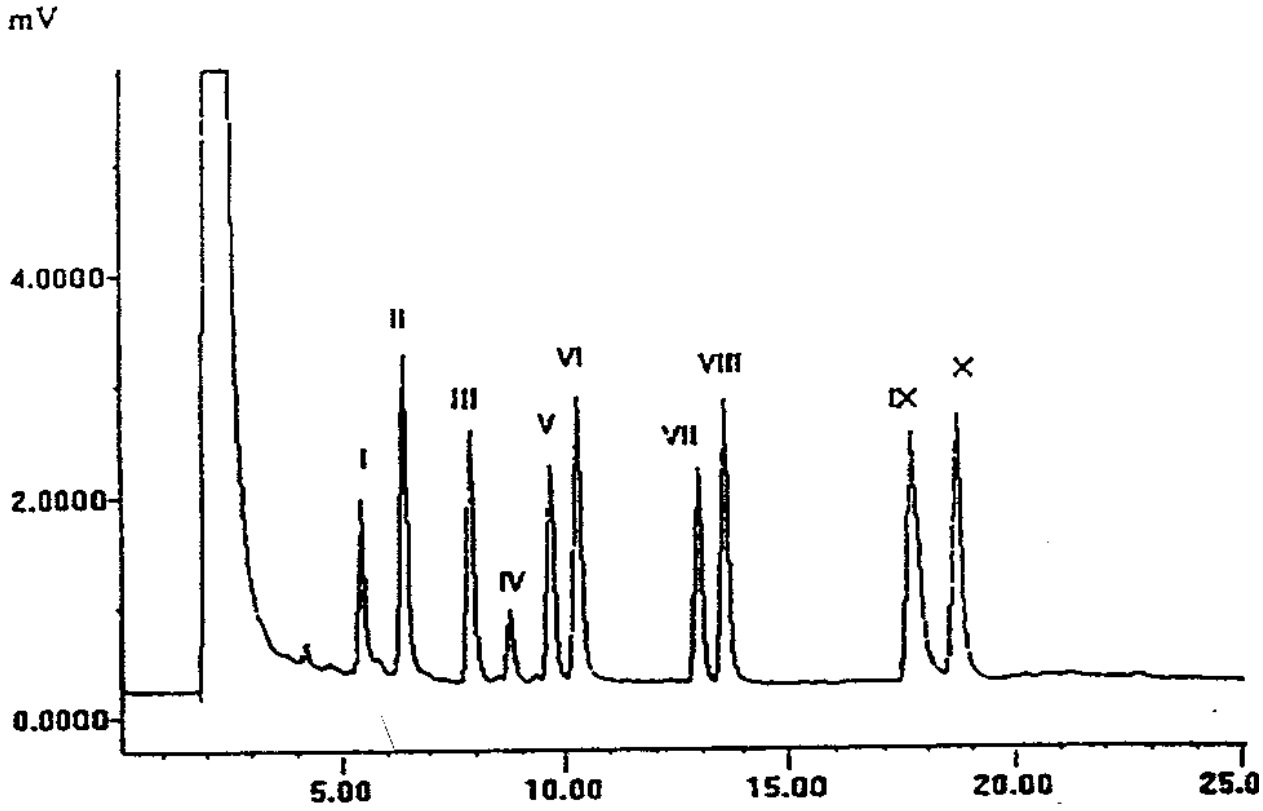
NOTE If necessary, the peak area values should be corrected by the value obtained from the blank samples, see 7.1.2 to 7.1.4.

Construct the calibration graph by plotting peak area versus the concentration added to the test material.

Read the isocyanate concentration of the test sample solution (7.1.1) from the calibration graph by back extrapolation to the x-axis where the magnitude of the intercept is equal to the isocyanate concentration. By multiplying the extrapolated figure by the appropriate factor (8.1) the isocyanate concentration of the test sample can be obtained, expressed in milligrams of NCO per kilogram of polymer.

Alternatively, the isocyanate concentration of the test sample solution can be determined mathematically by least squares regression.

Annex B
(informative)



Key

I Phenyl isocyanate
II Cyclohexyl isocyanate
III 1-Napthyl isocyanate
IV 2,4-Toluene diisocyanate
V 2,6-Toluene diisocyanate
VI 1,5-Napthalene diisocyanate
VII Diphenylmethane-4,4'- diisocyanate
VIII Diphenylmethane-2,4'- diisocyanate
IX Hexamethylene diisocyanate
X 2,4 Toluene diisocyanate dimer

Figure B.1 — Typical HPLC trace for standard isocyanate

Annex C
(informative)

Suggested gradient profile

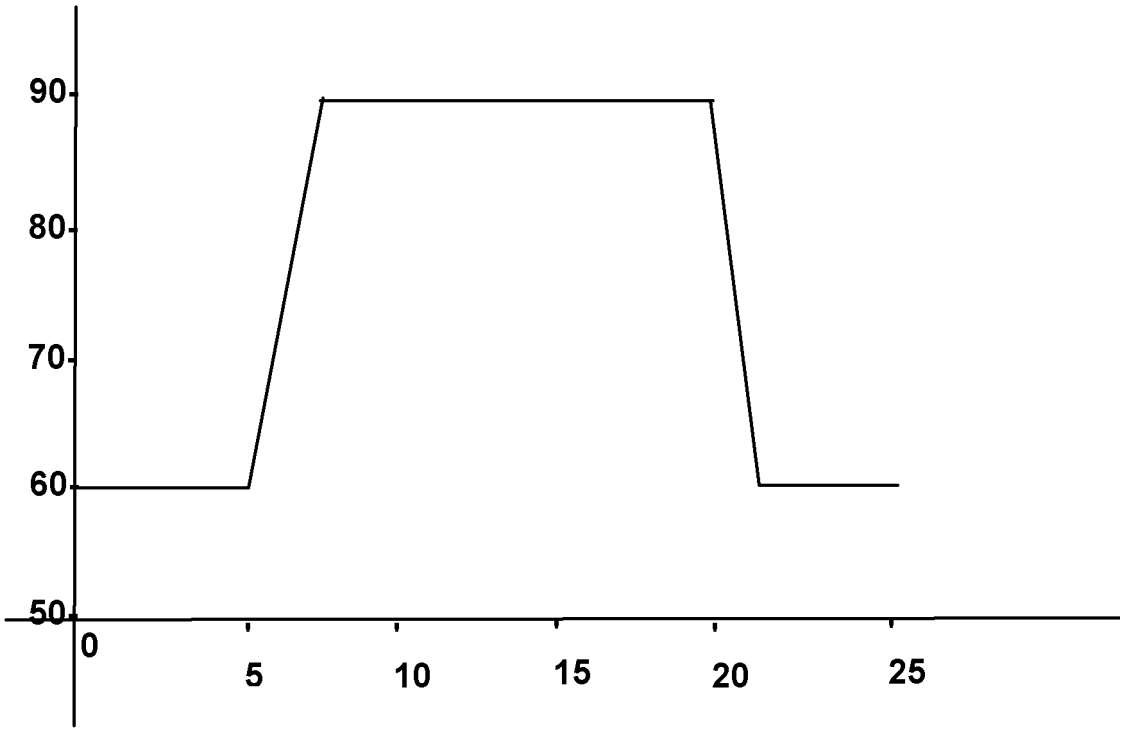


Figure C.1 - Suggested gradient profile

Bibliography

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic methods for the determination of repeatability and reproducibility of a standard measurement method*

[1] Commission of the European Communities, Commission Directive 2002/72/EC of 6 August 2002 relating to plastics materials and articles intended to come into contact with foodstuffs, Official Journal of the European Communities, 15 August 2002, no. L 220, p18.

[2] Commission of the European Communities, Council Directive of 21 December 1988 on the approximation of the laws of the Member States relating to materials and articles intended to come into contact with foodstuff (89/109/EEC), Official Journal of the European Communities, 11 February 1989, no. L 40, p 38.

[3] Commission of the European Communities, Council Directive of 18 October 1982 laying down the basic rules necessary for testing migration of the constituents of plastics materials and articles intended to come into contact with foodstuffs (82/711/EEC), Official Journal of the European Communities, 23 October 1982, no. L 297, p 26.

[4] Commission of the European Communities, Commission Directive of 15 March 1993 amending Council Directive 82/711/EEC laying down the basic rules necessary for testing migration of the constituents of plastics materials and articles intended to come into contact with foodstuffs (93/8/EEC), Official Journal of the European Communities, 14 April 1993, no. L 90, p 22.

[5] Commission of the European Communities, Commission Directive of 97/48/EC of 29 July 1997 amending Council Directive 82/711/EEC laying down the basic rules necessary for testing migration of the constituents of plastics materials and articles intended to come into contact with foodstuffs, Official Journal of the European Communities, 12 August 1997, no. L 222, p 10.

[6] Commission of the European Communities, Council Directive of 19 December 1985 laying down the list of simulants to be used for testing migration of constituents of plastics materials and articles intended to come into contact with foodstuffs (85/572/EEC), Official Journal of the European Communities, 31 December 1985, no. L372, p14.

[7] DIN 32645; Chemical analysis; decision limit; detection limit and determination limit; estimation in case of repeatability; terms, methods, evaluation.

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover. Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001. Fax: +44 (0)20 8996 7001. Email: orders@bsi-global.com. Standards are also available from the BSI website at http://www.bsi-global.com.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre. Tel: +44 (0)20 8996 7111. Fax: +44 (0)20 8996 7048. Email: info@bsi-global.com.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: +44 (0)20 8996 7002. Fax: +44 (0)20 8996 7001. Email: membership@bsi-global.com.

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsi-global.com/bsonline.

Further information about BSI is available on the BSI website at http://www.bsi-global.com.

Copyright

Copyright subsists in all BSI publications. BSI also holds the copyright, in the UK, of the publications of the international standardization bodies. Except as permitted under the Copyright, Designs and Patents Act 1988 no extract may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, photocopying, recording or otherwise – without prior written permission from BSI.

This does not preclude the free use, in the course of implementing the standard, of necessary details such as symbols, and size, type or grade designations. If these details are to be used for any other purpose than implementation then the prior written permission of BSI must be obtained.

Details and advice can be obtained from the Copyright & Licensing Manager. Tel: +44 (0)20 8996 7070. Fax: +44 (0)20 8996 7553. Email: copyright@bsi-global.com.

BSI
389 Chiswick High Road
London
W4 4AL