

Water quality — Determination of alkalinity —

Part 2: Determination of carbonate alkalinity

The European Standard EN ISO 9963-2:1995 has the status of a
British Standard

ICS 13.060.40

Confirmed
July 2008

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods, upon which the following bodies were represented:

The Association of the Laboratory Supply Industry
 British Agrochemicals Association Ltd.
 British Ceramic Research
 British Gas plc
 British Soft Drinks Association Ltd.
 Chemical Industries' Association
 Convention of Scottish Local Authorities
 Department of the Environment (Water Directorate)
 Department of Trade and Industry (Laboratory of the Government Chemist)
 GAMBICA (BEAMA) Ltd.
 Industrial Water Society
 Institution of Water and Environmental Management
 National Rivers Authority
 Royal Society of Chemistry
 Soap and Detergent Industry Association
 Society of Chemical Industry
 Swimming Pool and Allied Trades Association Ltd.
 Water Companies Association
 Water Research Centre
 Water Services Association of England and Wales

This British Standard, having been prepared under the direction of the Health and Environment Sector Board, was published under the authority of the Standards Board and comes into effect on 15 April 1996

© BSI 08-1999

The following BSI references relate to the work on this standard:

Committee reference EH/3/2
 Draft for comment 92/53921

ISBN 0 580 25292 2

Amendments issued since publication

Amd. No.	Date	Comments

Contents

	Page
Committees responsible	Inside front cover
National foreword	ii
<hr/>	
Foreword	2
1 Scope	3
2 Normative references	3
3 Definition	3
4 Principle	3
5 Reagents	3
6 Apparatus	5
7 Sampling and sample treatment	5
8 Procedure	5
9 Expression of results	6
10 Test report	6
<hr/>	
Annex A (informative) Information on factors for the conversion of alkalinity values to alternative units	8
Annex B (informative) Bibliography	8
Annex ZA (normative) Normative references to international publications with their relevant European publications	8
<hr/>	
Figure 1 — Principle for absorption of carbon dioxide from air	4
<hr/>	
Table 1 — Precision data	6
Table 2 — Comparison of results using this method with other methods for the determination of alkalinity	7
Table A.1	8
<hr/>	
List of references	Inside back cover

National foreword

This British Standard has been prepared by Subcommittee EH/3/2 and is the English language version of EN ISO 9963-2:1995 *Water quality — Determination of alkalinity — Part 2: Determination of carbonate alkalinity*, published by the European Committee for Standardization (CEN). It is identical with ISO 9963-2:1994, published by the International Organization for Standardization (ISO).

Cross-references

Publication referred to	Corresponding British Standard
ISO 3696:1987	BS 3978:1987 <i>Specification for water for laboratory use</i> BS EN 25667 <i>Water quality — Sampling</i>
EN 25667-1:1993 (ISO 5667-1:1980)	Part 1:1994 <i>Guidance on the design of sampling programmes</i>
EN 25667-2:1993 (ISO 5667-2:1991)	Part 2:1993 <i>Guidance on sampling techniques</i>
	BS 6068 <i>Water quality</i> Part 1 <i>Glossary</i>
ISO 6107-2:1989	Section 1.2:1990 <i>Additional terms relating to types of water, and treatment and storage of water and waste water, and terms used in sampling and analysis of water</i>
ISO 9963-1:1994	BS EN ISO 9663 <i>Water quality — Determination of alkalinity</i> Part 1 <i>Determination of total and composite alkalinity</i>
IEC 746-2:1982	BS 6438 <i>Electrochemical analyzers</i> Part 2:1984 <i>Method for specifying performance of pH value analyzers</i>

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN ISO title page, pages 2 to 8, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

ICS 13.060.40

Descriptors: Water, quality, water tests, chemical analysis, determination, alkalinity, volumetric analysis

English version

Water quality — Determination of alkalinity — Part 2: Determination of carbonate alkalinity

(ISO 9963-2:1994)

Qualité de l'eau — Détermination de
l'alcalinité — Partie 2: Détermination de
l'alcalinité carbonatée
(ISO 9963-2:1994)

Wasserbeschaffenheit — Bestimmung der
Alkalinität — Teil 2: Bestimmung der
Carbonatalkalinität
(ISO 9963-2:1994)

This European Standard was approved by CEN on 1995-10-11. 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, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Foreword

The text of the International Standard from ISO/TC 147, Water quality, of the International Organization for Standardization (ISO) has been taken over as a European Standard by the Technical Committee CEN/TC 230, Water analysis.

This European Standard consists of the following Parts:

EN ISO 9963-1, *Determination of total and composite alkalinity.*

EN ISO 9963-2, *Determination of carbonate alkalinity.*

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 June 1996, and conflicting national standards shall be withdrawn at the latest by June 1996.

According to the CEN/CENELEC Internal Regulations, the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom.

NOTE Normative references to International Standard are listed in Annex ZA (normative).

1 Scope

This part of ISO 9963 specifies a method for the titrimetric determination of carbonate alkalinity in natural and drinking water. Using a higher pH value for the endpoint than the method specified in ISO 9963-1, the influence of other hydrogen acceptors, such as anions of humic acids, is reduced by the procedure.

The method is intended for samples with a carbonate alkalinity between 0,01 mmol/l and 4 mmol/l (as H⁺ equivalents). For samples containing higher concentrations of alkalinity, a smaller test portion can be used for analysis.

In this context, carbonate alkalinity is often called total alkalinity and usually has nearly the same numerical value as methyl orange alkalinity (MO-alkalinity).

The endpoint detection, using a pH-meter is less prone to interferences than the use of the indicator.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 9963. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 9963 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

ISO 6107-2:1989, *Water quality — Vocabulary — Part 2*.

ISO 9963-1:1994, *Water quality — Determination of alkalinity — Part 1: Determination of total and composite alkalinity*.

IEC 746-2:1982, *Expression of performance of electrochemical analyzers — Part 2: pH value*.

3 Definition

For the purposes of this part of ISO 9963, the following definition applies.

3.1

alkalinity (A)

the quantitative capacity of aqueous media to react with hydrogen ions [ISO 6107-2]

in this method, the endpoint is chosen in such a way as to permit the full neutralization of the carbonate system

$$A = c(\text{HCO}_3^-) + 2c(\text{CO}_3^{2-}) + c(\text{OH}^-) + c(\text{X}) - c(\text{H}^+)$$

usually proton acceptors (X) other than the carbonate system are present in low concentrations and can often be disregarded. Examples of such buffering substances are ammonia, phosphate, and anions of humic and other organic acids

4 Principle

Alkalinity is determined by titration with hydrochloric acid, with simultaneous removal of carbon dioxide. In this way, a precise endpoint independent of the initial concentration of alkalinity can be used. The endpoint preferably needs to be as close to neutrality as possible but still low enough to allow the removal of carbon dioxide produced. In this part of ISO 9963, the endpoint is set at pH 5,4, since the pH value can easily be determined with the indicator chosen. The induced systematic error is corrected by titrating a blank.

5 Reagents

Use only reagents of recognized analytical grade.

Commercially available, ready-made solutions may be used.

5.1 Water, grade 2 in accordance with ISO 3696, free of interfering concentrations of acid or alkali and with a conductivity of less than 0,1 mS/m.

5.2 Gas, free from carbon dioxide, nitrogen or alternatively a gas free from carbon dioxide obtained by passing air through a standing tube filled with soda lime or another compound that absorbs carbon dioxide. Then pass the gas through a wash bottle containing water and subsequently the gas distribution tube (see Figure 1).

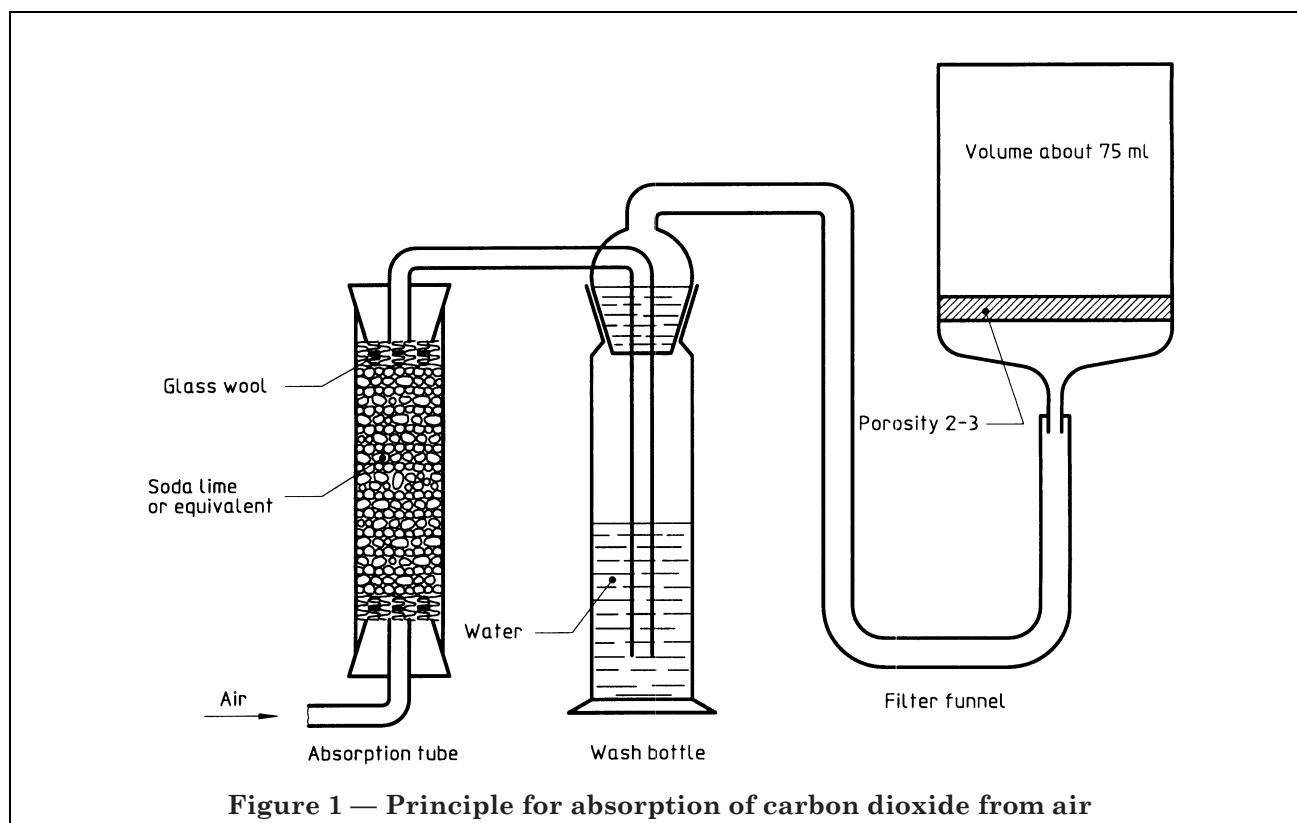


Figure 1 — Principle for absorption of carbon dioxide from air

5.3 Mixed indicator pH 5,4

Dissolve 0,040 g \pm 0,005 g of methyl red and 0,060 g \pm 0,005 g of bromocresol green in 100 ml of ethanol [$> 90\%$ (V/V)]. Neutralize the solution with about 2 ml of 0,1 mol/l sodium hydroxide until a brown colour appears. Check the neutrality of the indicator solution by titration to endpoint of one sample. If the brown colour does not remain after the addition of 10 more drops of the indicator, adjust the pH of the indicator solution. Stored in an amber glass bottle, the solution is stable for at least 6 months.

Sodium carbonate solution, $c(\text{Na}_2\text{CO}_3) \approx 0,025$ mol/l.

Dry sodium carbonate (Na_2CO_3) in an oven at $250\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$ for 4 h. Allow to cool in a desiccator. Dissolve 1,3 g \pm 0,1 g (weighed to the nearest 0,001 g) in water in a 500 ml volumetric flask.

This solution is stable for at least one month if stored in a refrigerator.

5.4 Hydrochloric acid, $c(\text{HCl}) \approx 0,020$ mol/l.

Dilute 1,7 ml \pm 0,1 ml of concentrated hydrochloric acid ($\rho \approx 1,18$ g/ml) to 1 000 ml with water in a volumetric flask.

An equivalent, commercially available solution can be used.

Standardize this solution at least weekly as follows.

Pipette 2,00 ml \pm 0,02 ml of the sodium carbonate solution () into the titration vessel (6.2) and add 40 ml \pm 5 ml of water (5.1). Titrate according to the procedure using electrodes (see 8.1) or with indicator (8.2) for the endpoint detection

Perform at least three titrations, and record the volumes (V_2) of hydrochloric acid consumed. The difference between the highest and lowest volume of hydrochloric acid consumed shall be less than 0,05 ml. Continue until three consecutive titrations give the required result. Using $50 \text{ ml} \pm 5 \text{ ml}$ of water (5.1), carry out a blank determination in the same manner and note the volume V_3 , in millilitres, of acid consumed.

Calculate the concentration of the hydrochloric acid using the equation

$$c(\text{HCl}) = \frac{2mV_1}{53,00(V_2 - V_3)}$$

where

- $c(\text{HCl})$ is the concentration, expressed in moles per litre, of the hydrochloric acid solution (5.4);
- m is the mass, in grams, of sodium carbonate taken for the preparation of solution ;
- V_1 is the volume, in millilitres, of sodium carbonate solution () taken for titration (normally 2,0 ml);
- V_2 is the volume, in millilitres, of hydrochloric acid solution (5.4) consumed in the titration of the sodium carbonate solution ();
- V_3 is the volume, in millilitres, of hydrochloric acid solution (5.4) consumed in the blank titration.

6 Apparatus

Usual laboratory equipment and, in particular, the following should be used.

6.1 Burette, preferably of total capacity 10 ml, graduated in divisions of 0,02 ml, and conforming to the requirements of ISO 385-1.

6.2 Titration vessel, use either a glass filter funnel with a porosity of 2-3 and a volume of about 75 ml, or a gas distribution tube for dipping into the titration vessel (an Erlenmeyer flask with a volume of 100 ml).

6.3 pH-meter, with a compatible electrode system suitable for the measurement of pH to within $\pm 0,05$ pH units over the range 3 to 10, for use when the endpoint determination is to be made using a pH-meter. The equipment shall be set up, calibrated, and used according to IEC 746-2.

Alternatively, a titrator fulfilling these specifications can be used.

7 Sampling and sample treatment

Collect samples in clean polyethylene or borosilicate glass bottles with a volume of at least 100 ml. Fill the bottle completely with the sample and insert the stopper so that no air remains inside the bottle. Analyse the samples immediately after collection. If this is not possible, store the samples at a temperature of $4 \text{ }^\circ\text{C}$ to $8 \text{ }^\circ\text{C}$ in order to avoid nitrification or scaling. (See ISO 5667-2.)

8 Procedure

Mount the components according to Figure 1.

NOTE 1 Coloured samples interfere with the indicator endpoint determination. Such samples should be analysed using a pH-meter.

8.1 Endpoint detection with a pH-meter

Set the gas flow (5.2) to the titration vessel (6.2) at a rate that produces abundant bubbles and transfer $50,0 \text{ ml} \pm 0,1 \text{ ml}$ of sample (volume V_4) to the vessel. Insert the pH electrodes and titrate slowly with hydrochloric acid (5.4) to a pH value of 5,4. The pH value has to be stable for at least 30 s, if not continue the titration. Note the volume V_5 , in millilitres, of acid consumed.

If the volume of acid consumed exceeds 10 ml, take a smaller volume of the sample (V_4) and dilute to $50 \text{ ml} \pm 5 \text{ ml}$ with water (5.1). In this case, the volume of acid consumed shall be not less than 3 ml.

8.2 Endpoint detection with indicator

Set the gas flow (5.2) to the titration vessel (6.2) at a rate that produces abundant bubbles and transfer $50,0 \text{ ml} \pm 0,1 \text{ ml}$ of sample (volume V_4) to the vessel. Add three drops of indicator and titrate slowly with hydrochloric acid (5.4) until the colour changes to grey with a trace of red. The colour has to remain for at least 30 s, if not continue the titration. Note the volume V_5 , in millilitres, of acid consumed.

If the volume of acid consumed exceeds 10 ml, take a smaller portion of the sample and dilute to $50 \text{ ml} \pm 5 \text{ ml}$ with water (5.1). In this case, the volume of acid consumed shall be not less than 3 ml.

8.3 Blank sample

Titrate 50 ml of water (5.1) in the same way as for the sample. Perform at least three titrations and calculate the mean value (volume V_6).

9 Expression of results

9.1 Calculation

Calculate the concentration of alkalinity, expressed in millimoles per litre, using the equation

$$A = \frac{c(\text{HCl})(V_5 - V_6) \times 1\,000}{V_4}$$

where

- A is the alkalinity of the sample, expressed in millimoles per litre;
- $c(\text{HCl})$ is the concentration, expressed in moles per litre, of the hydrochloric acid (5.4);
- V_4 is the volume, in millilitres, of the sample;
- V_5 is the volume, in millilitres, of hydrochloric acid (5.4) consumed by the sample;
- V_6 is the volume, in millilitres, of hydrochloric acid (5.4) consumed by the blank sample (8.3).

Report the result, expressed in millimoles per litre, to two significant digits.

9.2 Precision

Two interlaboratory tests performed in 1988 and 1992 gave the results shown in Table 1.

In two international interlaboratory calibrations this method was used by one laboratory, with the results shown in Table 2.

At one laboratory, a control solution with a concentration of 0,200 mmol/l gave a mean value of 0,201 mmol/l and a coefficient of variation of 2,0 % (number of measuring values = 49).

10 Test report

The test report shall include the following information:

- a) a reference to this part of ISO 9963;
- b) precise identification of the sample;
- c) the result, expressed in millimoles per litre to two significant digits;
- d) the endpoint detection used;
- e) any departure from the procedure specified or any other circumstance that may have affected the results.

Table 1 — Precision data

Type of water	Reference	Number of laboratories	Number of outliers	Mean concentration mmol/l	Coefficient of variation %
Drinking water	SNV 3535	70	2	2,984	3,6
		69	3	4,480	3,6
		69	4	0,933	4,0
Natural water	ITM 1993	100	2	1,142	3,4
		101	1	0,884	3,4
		100	1	1,406	3,0
		101	1	1,118	3,5

Table 2 — Comparison of results using this method with other methods for the determination of alkalinity

Type of water	Reference	Number of laboratories	Number of outliers	Concentration, mmol/l	
				This method	All methods
9105	NIVA 1991	20	1	0,298	0,300
Sample A					
Sample B	20	1	0,358	0,358	
9206	NIVA 1992	20	13	0,042	0,047
Sample A					
Sample B	20	13	0,151	0,155	

Annex A (informative)**Information on factors for the conversion of alkalinity values to alternative units**

Alkalinity values may be expressed in alternative units. Factors for the conversion from millimoles per litre are given in Table A.1.

Table A.1

Alternative unit for the expression of results	Conversion factor
mmol/l CaCO ₃	0,50
mg/l CaCO ₃	50
English degree (= 1 Clark degree)	3,50
German degree	2,80
French degree	5,0
U.S. degree	2,90

Annex B (informative)**Bibliography**

- [1] Convention on long-range transboundary air pollution, *Intercalibration 9105*. Programme Centre, Norwegian Institute for Water Research, Oslo.
- [2] Convention on long-range transboundary air pollution, *Intercalibration 9206*. Programme Centre, Norwegian Institute for Water Research, Oslo.
- [3] STUMM, W. and MORGAN, J.J. *Aquatic Chemistry*. J. Wiley (1981).
- [4] ITM 1993. Comparison of testing 1992-1. Ion balance. (In Swedish with English summary.) Institute of Applied Environmental Research, University of Stockholm, Sweden.
- [5] SNV 3535. Intercalibration 1988-1. Chemical analysis of drinking water. (In Swedish with English summary.) Swedish National Environmental Protection Agency.

Annex ZA (normative)**Normative references to international publications with their relevant European publications**

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).

Publication	Year	Title	EN	Year
ISO 5667-1	1980	<i>Water quality — Sampling — Part 1: Guidance on the design of sampling programmes</i>	EN 25667-1	1993
ISO 5667-2	1991	<i>Water quality — Sampling — Part 2: Guidance on sampling techniques</i>	EN 25667-2	1993

List of references

See national foreword.

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: 020 8996 9000. Fax: 020 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: 020 8996 9001. Fax: 020 8996 7001.

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: 020 8996 7111. Fax: 020 8996 7048.

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: 020 8996 7002. Fax: 020 8996 7001.

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.

If permission is granted, the terms may include royalty payments or a licensing agreement. Details and advice can be obtained from the Copyright Manager. Tel: 020 8996 7070.