



COMMISSION OF THE EUROPEAN COMMUNITIES

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Proposal for a

REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

on Detergents

(presented by the Commission)

EXPLANATORY MEMORANDUM

Article 1. – Objectives

The fundamental objective of this Regulation is the free movement of detergents in the Internal Market. In particular it modernises the existing detergent directives, regarding the biodegradability of surfactants and the protection of the environment in relation to this fundamental issue. The proposed new biodegradability tests ensure a higher level of environmental protection and at the same time are applicable to all types of surfactants in detergents. Furthermore, the requirements specified in Commission Recommendation 89/542, on labelling of detergents and cleaning products, and specific information to the consumers related to the presence in detergents of fragrance substances are made binding for the products covered by this Regulation.

Article 2 and Annex I. – Definitions

The definition proposed for “detergent” enlarges the scope of the existing legislation to cover other similar uses, which come within the objectives of this legislation in line with relevant experiences in implementation in Member States.

It introduces a definition for surfactants, which was lacking in existing legislation.

Definitions are provided for the biodegradation concepts involved in the Regulation, as these are useful for a correct implementation of its provisions.

Finally, other definitions (*i.e.*: “cleaning”, “washing”, “substance”, “preparation”, “placing on the market”, etc.) that may be useful for the application of this Regulation are also considered.

Articles 3 to 7. – Limitations to placing on the market

These articles refer explicitly to the requirements for the prohibition of substances on the market and to the conditions for the granting of derogations.

It is considered appropriate to establish a transition period of two years, counting from the date of implementation of the Regulation, to allow manufacturers (a term which in this text extends to include importers) of those substances concerned to apply for derogations.

The hierarchy of tests is based on environmental concerns and at the same time tries to minimise the expenses of economic operators as only a fraction of the substances concerned will have to be submitted to the whole array of relevant tests. This would be needed just for those substances.

The granting of derogations for those substances failing the “ultimate biodegradability” type tests as established in Annex III, are to be allowed following explicit application by manufacturers and case by case Commission Decisions adopted by Committee procedure.

The granting of derogations needs as a pre-requisite the compliance with the primary biodegradability requirements in Annex II, and depends on the assessment of the additional information to be provided under Annex IV.

It has been considered appropriate to refer in this article to other legislation, in particular Directive 76/769/EEC, by which substances covered in this Regulation might be the object of

marketing restrictions, as for example those in connection with Parcom Decisions or Recommendations.

It is intended that there should be a shift of emphasis of responsibility towards manufacturers who would have to ensure that all pertinent tests are carried out, instead of the present situation that depends much on Member States initiatives.

Article 8. – Duties of the Member States

It is considered fundamental for the objectives of the Regulation to establish with precision the main actions involving direct responsibility of the appointed competent authorities in Member States in addition to those stipulated in Article 3 concerning the limitations to the placing on the market.

As in the preceding legislation, Member States should notify the list of Laboratories authorised to carry out the reference tests as established in Annexes II and III.

Article 9. – Duties of Manufacturers

Manufacturers of detergents, and/or of surfactants for detergents, should have at the disposal of the national authorities the corresponding technical files for all substances concerned. Member states should take all appropriate measures including active actions in order to ensure this provision is complied with.

Manufacturers of detergents remain responsible for not marketing detergent preparations containing non-complying surfactants and for ensuring that all the required technical documentation is available.

Article 10. – Control measures

The competent authorities of Member States should have the possibility of applying control measures to ensure that manufacturers comply with this Regulation.

Article 11 and Annex VIII. – Labelling and ingredient datasheet

This article together with the corresponding Annex keep the existing provisions on labelling as they are to be continued. At the same time and in order to take account of the development introduced by Commission Recommendation 89/542/EEC for the labelling of detergents and cleaning products, its provisions as established in Articles 2 and 3 are made binding.

The Recommendation has worked well in the sense that there has been a high level of compliance in most Member States. However, the present proposal is a useful opportunity to combine the labelling rules with other rules on the marketing of detergents.

This transition should be considered as a success of the Recommendation and it is by no means to be interpreted as an approach against voluntary agreements. The Commission Recommendation 98/480/EC, concerning good environmental practice for household laundry detergents, will remain separate as it concerns areas not covered by this Regulation.

In the light of the increasing importance of fragrances and preservation agents, they are included as a new element in relation to Recommendation 89/542/EEC.

A new provision is added obliging manufacturers of detergents to have at the disposal of health care professionals a full listing of the ingredients of the detergents to assist clinicians in investigating whether a causal link exists between the development of an allergic response and exposure to a particular chemical substance.

Article 12. – Committee procedure

The Committee procedure proposed is a regulatory one, as established under the new Decision 1999/468/EC.

Article 13. – Adaptation of the annexes

It is proposed that the revision of Annexes I to IX should follow the Committee procedure, as these relate to scientific and technical matters and do not touch the fundamental hierarchy established in the body of the Regulation.

The Committee procedure should also apply to Articles 4, 5, 7, 8 and 13 which are linked to the placing on the market of substances and preparations.

Article 14. – Free movement clause

This is the explicit complement to the clauses on limitations to marketing and covers those substances and preparations that are complying with the provisions of the Regulation.

Article 15. – Safeguard clause

The fact that a substance is found to be readily biodegradable does not preclude the possibility of concern for the degradation products and biodegradation rates in relation to certain types of uses, in particular, in cases of high influx into ecosystems.

Article 16. – Legislation to be replaced

This establishes which directives are to be superseded by the present Regulation that covers their relevant provisions.

Article 17. – Sanctions for non-compliance

This requires the Member States to establish sanctions for non-compliance with this Regulation.

Annex I. – Products covered within the meaning of detergent

This lists the products containing soap or other surfactants that are covered by the new definition of detergent as set out in Article 2 and gives also a definition of them.

Annex II. – Primary biodegradability test methods

This establishes the test systems and analytical methods for assessing the primary biodegradability of surfactants: anionic, non-ionic, cationic, and amphoteric.

The main changes in relation to the methods in the existing legislation are intended to cover for the first time cationic and amphoteric surfactants and also those anionic and non-ionics not reacting to the tests included in present legislation. The use of instrumental analysis for those

surfactants not reacting to semi-specific methods is required so that all surfactants are covered.

These tests will be relevant in cases of non-compliance with those on “ultimate” biodegradability in Annex III, and they will be examined by the Committee on a case by case basis. It has been considered better to keep the present choice of options on primary biodegradability tests, but the reference methods for the cases of conflicting results in different Member States are stipulated. These tests will also be necessary for calculating the predicted environmental concentrations of the parent substance for risk assessment.

Annex III. – “Ultimate biodegradability” test methods

The approach presented is based on Annex V part C.4 (Determination of “ready” biodegradability) of Directive 67/548/EEC.

However, account is taken of the need to adapt to scientific progress the test chosen for reference purposes as developed by ISO.

The use of some tests not considered well suited, in general, for surfactants is made dependent of specific authorisation by Committee procedure.

The study “Surfactant Ring Test-I” of May 1999 (WRC) concluded that pre-exposing sludge to a surfactant for seven days in a SCAS unit before testing the surfactant in the headspace method did not have uniform effects on the biodegradation achieved or on its variability, although in general the degree of biodegradation was increased. Taking results from all laboratories it is not worthwhile using this rather mild pre-exposure since it involves a fair amount of effort for little advantage.

The proposed Annex III is also fully in line with the recommendations included in the opinion of the CSTEE, which may be summarised as follows:

1. The proposed “ultimate biodegradability” type tests are an improvement in relation to primary biodegradability;
2. The methods ISO headspace, OECD 301 B¹ and OECD 301 D² are suitable but the two OECD methods had some limitations of applicability;
3. The methods OECD 301 A³, OECD 301 C⁴, OECD 301 E⁵ and OECD 301 F⁶ were less suitable than the above mentioned;
4. Pre-adaptation is not deemed desirable;
5. The ten days window is not deemed desirable.

The test methods of Annex III are therefore the best of the available standardised test methods for ‘ultimate biodegradability’. They are also more demanding than those for primary

¹ Method Directive 67/548/EEC, Annex V.C.4.C.

² Method Directive 67/548/EEC, Annex V.C.4.E.

³ Method Directive 67/548/EEC, Annex V.C.4.A.

⁴ Method Directive 67/548/EEC, Annex V.C.4.F.

⁵ Method Directive 67/548/EEC, Annex V.C.4.B.

⁶ Method Directive 67/548/EEC, Annex V.C.4.D.

biodegradability that are used in the current EU legislation. It is estimated that 3 % of the surfactants that are capable of passing the test for primary biodegradability under current EU legislation would not pass the test specified for the ‘ultimate biodegradability’ in Annex III. Besides being stricter than the existing test, the new test also covers a significant market segment composed of cationic and amphoteric surfactants, representing about 10 % of all detergent surfactants, that were not previously covered by the existing tests.

Annex IV. – Complementary Risk Assessment

This establishes the additional information needed for substances failing Annex III tests but passing Annex II tests and being submitted for derogation under Article 3(3).

Council Regulation (EEC) No 793/93 on the evaluation and control of the risks of existing substances laid down detailed rules concerning the collection, circulation and accessibility of information on existing substances, as well as concerning the evaluation of the risks of existing substances to man and to the environment in order to ensure better management of those risks within the framework of Community provisions.

Evaluation of risks before the placing on the market of new substances according to agreed procedures is another type of programmed assessment. Such an evaluation and an appropriate notification to a competent authority before the placing on the market are required for chemicals by Directive 92/32/EEC amending for the seventh time Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to classification, packaging and labelling of dangerous substances. Plant protection products and other biocides also have to pass thorough risk evaluation before they can receive an authorisation to be commercialised.

The approach envisaged here is to establish an ad-hoc complementary assessment not intended to be closely parallel to the risk assessment procedure in the two above mentioned pieces of legislation. Instead, the intention of the complementary assessment step is to assess the reasons for failing the first level stage and the opportunity to allow marketing (provided that primary biodegradability is complied with).

It is to be considered that in any event these would apply to the substances covered by the future detergent Regulation when so stipulated.

It is to be considered that detergents and their ingredients are also covered by all the horizontal legislation on substances and preparations and the corresponding risk assessments.

Following this line, the chosen approach is to concentrate on the elements helping to judge whether a negative result on “ready biodegradability” type tests is a false negative and to provide also a number of other elements considered essential to judge the environmental impact of the surfactant in question and of its biodegradation products.

Account is taken of the Recommendations in the opinion of the CSTEE, so that the risk assessment should put emphasis on possible metabolites and that information on the toxicity of these metabolites is needed together with their bioconcentration potential, as well as their partition to the sediment phase. It is emphasised that if recalcitrant metabolites are produced, a risk assessment should be performed, according to the relevant EU legislation on dangerous substances and to the related Technical Guidance Documents. Moreover, if some metabolites are suspected for endocrine disrupting activity, it is recommended to have data on this particular hazard, as soon as validated protocols to assess this kind of effect will be available.

Annex V. – List of derogations

This lists all the surfactants obtaining derogations.

Annex VI. – List of banned or restricted surfactants under this Regulation

This lists all the surfactants identified as not complying with the provisions of this Regulation or restricted in use as a result of this Regulation.

Annex VII. – List of banned surfactants in implementation of other Community legislation

This lists surfactants covered by this Regulation and banned or restricted by other Community legislation, in particular Directive 76/769/EEC.

Annex VIII. – Labelling and ingredient datasheet

This describes how detergent packaging shall be labelled for certain ingredients, for the recommended quantities of detergent appropriate for a standard washing machine load, and for the number of standard washing machine loads that can be washed with the contents of the package. It also prescribes the format to be used for the listing of ingredients on the datasheet intended for health care professionals.

Annex IX. – List of test methods and analytical methods

This lists the test methods and analytical methods that apply to control procedures of detergents on the market by Member States, which were annexed to the existing detergent legislation.

Proposal for a

REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

on Detergents

(Text with EEA relevance)

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 95 thereof,

Having regard to the proposal from the Commission ⁷,

Having regard to the opinion of the Economic and Social Committee ⁸,

Acting in accordance with the procedure laid down in Article 251 of the Treaty ⁹,

Whereas:

- (1) Council Directive 73/404/EEC of 22 November 1973 on the approximation of the laws of the Member States relating to detergents ¹⁰ as last amended by Council Directive 86/94/EEC ¹¹, Council Directive 73/405/EEC of 22 November 1973 on the approximation of the laws of the Member States relating to methods of testing the biodegradability of anionic surfactants ¹² as last amended by Council Directive 82/243/EEC ¹³, and Council Directive 82/242/EEC of 31 March 1982 on the approximation of the laws of the Member States relating to methods of testing the biodegradability of non-ionic surfactants and amending Council Directive 73/404/EEC ¹⁴, for reasons of clarity and efficiency, should be modernised and replaced by a single text; and labelling provisions concerning detergents and cleaning products of Commission Recommendation 89/542/EEC of 13 September 1989 for the labelling of detergents and cleaning products ¹⁵ are to be included;
- (2) In accordance with the principles of subsidiarity and of proportionality, as stated in Article 5 of the Treaty, the objectives of the envisaged action to ensure the internal market in detergents cannot be achieved individually by Member States if there are no common technical criteria throughout the Community, and can therefore be better

⁷ OJ C , ... , p. .

⁸ OJ C , ... , p. .

⁹ Opinion of the European Parliament of .

¹⁰ OJ L 347, 17.12.1973, p. 51.

¹¹ OJ L 80, 25.3.1986, p. 51.

¹² OJ L 347, 17.12.1973, p. 53.

¹³ OJ L 109, 22.4.1982, p. 18.

¹⁴ OJ L 109, 22.4.1982, p. 1.

¹⁵ OJ L 291, 10.10.1989, p. 55.

achieved by Community action; this action should be limited to the minimum required to achieve these objectives and should not exceed what is necessary to this end; a Regulation is the appropriate legal instrument as it imposes directly on manufacturers precise requirements to be implemented at the same time and in the same manner throughout the Community; in the area of technical legislation, uniformity of application in the Member States is needed, and this can only be guaranteed by a Regulation;

- (3) A new definition for detergents is needed to cover equivalent uses and be in line with developments at Member State level;
- (4) It is necessary to introduce a surfactant definition, which was lacking in the existing legislation;
- (5) It is important to give a clear and precise description of the relevant types of biodegradability;
- (6) Measures concerning detergents should be adopted to ensure the functioning of the internal market and avoid restricting the competition in the Community;
- (7) As confirmed by the *Commission White Paper on the strategy for a future Chemical Policy*¹⁶ these measures should ensure a high level of environmental protection, especially of the aquatic environment;
- (8) Detergents are already subject to certain Community provisions concerning the manufacture, proper handling, usage and labelling, in particular with reference to Commission Recommendation 89/542/EEC and Commission Recommendation 98/480/EC of 22 July 1998 concerning good environmental practice for household laundry detergents¹⁷; Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations¹⁸ applies to detergents;
- (9) Ditolow-dimethyl-ammonium-chloride (DTDMAC) and Nonylphenol (including ethoxylates derivatives-APEs) are priority substances undergoing at Community level Risk Assessment activities, in accordance with Council Regulation (EEC) No 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances¹⁹, and if necessary adequate strategies to limit the risks of exposure to these substances will be recommended and implemented in the framework of other relevant EC instruments;
- (10) The existing legislation on biodegradability of surfactants in detergents only covers primary biodegradability²⁰ and it is only applicable to anionic²¹ and non-ionic²²

¹⁶ Document COM(2001) 88 final.

¹⁷ OJ L 215, 1.8.1998, p. 73.

¹⁸ OJ L 200, 30.7.1999, p. 1.

¹⁹ OJ L 84, 5.4.1993, p. 1.

²⁰ Council Directive 73/404/EEC (OJ L 347, 17.12.1973, p. 51) and Council Directive 86/94/EEC (OJ L 80, 25.3.1986, p. 51).

²¹ Council Directive 73/405/EEC (OJ L 347, 17.12.1973, p. 53) and Council Directive 82/243/EEC (OJ L 109, 22.4.1982, p. 18).

surfactants; therefore it needs to be replaced by new legislation, which lays the main emphasis on ultimate biodegradability and meets the important concerns related to the potential toxicity of persistent metabolites;

- (11) This requires the introduction of a new set of tests based on EN ISO standards and OECD guidelines, which governs the granting of direct permission for placing detergents on the market;
- (12) To provide a high level of protection of the environment, detergents not fulfilling requirements laid down by this Regulation, shall not be placed on the market;
- (13) On 25 November 1999 the Scientific Committee on Toxicity, Ecotoxicity and the Environment has issued an opinion on biodegradability of surfactants in detergents and relevance of test-methods for regulatory control in this area;
- (14) The existing requirements regarding primary biodegradability are to be maintained on a second hierarchy level for those surfactants failing “ultimate biodegradability” tests; furthermore surfactants failing primary biodegradability tests cannot obtain marketing authorisation by way of derogation;
- (15) The primary biodegradability requirements need to be extended to all surfactants, in particular cationic and amphoteric, whilst allowing the possibility of applying instrumental analyses in those cases in which semi-specific analytical methods are not suitable;
- (16) The determination of biodegradability test-methods, setting criteria for derogations, and the record-keeping of lists of derogations are technical matters, which need to be revised taking into account technical and scientific developments as well as regulatory developments;
- (17) Test-methods should produce data that give sufficient assurance of aerobic biodegradability of surfactants in detergents;
- (18) Test-methods to test biodegradability of surfactants in detergents may produce variable results and may need to be complemented by additional assessments in order to determine the risks of continued use;
- (19) Provisions should also be set out to place on the market in exceptional cases surfactants in detergents failing “ultimate biodegradability” tests and this should take place on the basis of all relevant information to ensure environmental protection and on a case by case basis;
- (20) Since the measures necessary for the implementation of this Regulation are measures of general scope within the meaning of Article 2 of Council Decision 1999/468/EC of 28 June 1999 laying down the procedures for the exercise of implementing powers conferred on the Commission²³, they should be adopted by use of the regulatory procedure provided for in Article 5 of that Decision;

²² Council Directive 82/242/EEC (OJ L 109, 22.4.1982, p. 1).

²³ OJ L 184, 17.7.1999, p.23.

- (21) It is appropriate to refer to other horizontal legislation applicable to detergent surfactants, in particular Council Directive 76/769/EEC of 27 July 1976 by which the marketing and use of dangerous substances covered by this Regulation might be banned or restricted²⁴, Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances²⁵, Commission Directive 93/67/EEC of 20 July 1993 on assessment of risks to man and the environment of new substances²⁶ or Regulation (EEC) No 793/93; and Commission Regulation (EC) No 1488/94 of 28 June 1994 laying down the principles for the assessment of risks to man and the environment of existing substances²⁷;
- (22) It should be the responsibility of manufacturers to refrain from marketing detergents not complying with the provisions of this Regulation and to have at the disposal of the national authorities the corresponding technical files for all substances and preparations covered by this Regulation; this should also apply to surfactants that have failed to pass the tests mentioned in Annex III;
- (23) Manufacturers should be able to request a derogation and the Commission should have the possibility to grant such derogation in accordance with the Committee procedure of this Regulation;
- (24) Member State competent authorities should be able to apply control measures to detergents on the market, but should avoid repeating tests made by the competent laboratories;
- (25) Labelling provisions should be continued, including those in Recommendation 89/542/EEC, for the labelling of detergents and cleaning products, which is included in order to fulfil the objective of modernising the rules on detergent products. Specific labelling is introduced to inform consumers about fragrance substances and preservation agents that are present in detergents. Health care professionals should be able to obtain from the manufacturer upon request a full listing of all ingredients of a detergent to assist them investigate whether a causal link exists between the development of an allergic response and exposure to a particular chemical substance;
- (26) All the above points call for new legislation replacing the existing legislation; however, for a period not exceeding eighteen months, Member States can continue to apply their existing laws;
- (27) The technical Annexes to this Regulation are to be adapted by Committee procedure;
- (28) Detergents complying with this Regulation should be allowed to be placed on the market without prejudice to other relevant Community provisions;
- (29) In order to ensure the protection of man and the environment from unforeseen risks of detergents, a safeguard clause is needed;

²⁴ OJ L 262, 27.9.1976, p. 201.

²⁵ OJ L 196, 16.8.1967, p. 1.

²⁶ OJ L 227, 8.9.1993, p. 9.

²⁷ OJ L 161, 29.6.1994, p. 3.

- (30) The tests specified for the biodegradability of surfactants should be carried out in laboratories meeting an internationally recognised standard, namely EN/ISO/IEC/17025; it would not be justified to ask for the application of this latter requirement to existing surfactants to the extent that the available tests on them had been performed before the entering into force of the above standard and still provide a comparable level of scientific quality;
- (31) The issues relating to anaerobic biodegradation, the biodegradation of the main non-surfactant organic detergent ingredients, and phosphate content should be reviewed by the Commission and, where this is justified, a proposal should be presented to the European Parliament and the Council;
- (32) The five Directives and the Commission Recommendation mentioned in recital 1 which are replaced by this Regulation should be repealed;

HAVE ADOPTED THIS REGULATION:

Article 1
Objectives and scope

1. This Regulation establishes rules designed to achieve the free movement of detergents and surfactants for detergents in the internal market while, at the same time, ensuring a high degree of protection of the environment.
2. For this purpose, this Regulation lays down rules for:
 - the biodegradability of surfactants in detergents and
 - the labelling of detergents.

Article 2
Definitions

For the purpose of this Regulation:

1. “Detergent” means any substance or preparation containing soaps or other surfactants intended for water-based washing processes. Detergents may be in any form (liquid, powder, paste, bar, cake, moulded piece, shape, etc.) and used for household, and/or institutional and/or industrial purposes. Other products to be considered as covered within the meaning of this definition are listed in Annex I.A;
2. “Washing” means the cleaning of laundry, fabrics, dishes or kitchen utensils;
3. “Cleaning” has the meaning defined by EN ISO 862;
4. “Substance” means chemical elements and their compounds in the natural state or obtained by any production process, including any additive necessary to preserve the stability of the products and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition;

5. “Preparation” means mixture or solution composed of two or more substances;
6. “Surfactant” means any organic substance and/or preparation used in detergents which is intentionally added to achieve cleaning, rinsing, fabric softening and/or any other purpose due to its surface-active properties, and which consists of one or more hydrophilic and one or more hydrophobic groups of such a nature and size that it is capable of forming micelles;
7. “Primary biodegradation” means the structural change (transformation) of a surfactant by micro-organisms resulting in the loss of its surface-active properties due to the degradation of the parent substance and consequential loss of the surface-active property as measured in test-methods listed in Annex II;
8. “Ultimate aerobic biodegradation” means the level of biodegradation achieved when the surfactant is totally used by micro-organisms in the presence of oxygen resulting in its breakdown to carbon dioxide, water and mineral salts of any other elements present (mineralisation) , as measured in tests methods listed in Annex III, and new microbial cellular constituents (biomass) ;
9. “Placing on the market” means introducing onto the Community market, thereby making available to third parties, whether in exchange for payment or not. Importation into the Community customs territory shall be deemed to be placing on the market;
10. “Manufacturer” means the natural or legal person (including importers) placing a detergent and/or a surfactant for detergents on the market.

Article 3

The placing on the market

1. Detergents and surfactants for detergents referred to in Article 1 shall conform with the conditions, characteristics and limits laid down in this Regulation and its Annexes when placed on the Community market.
2. Manufacturers of detergents and/or of surfactants for detergents shall be established within the Community.
3. Manufacturers shall be responsible for the conformity of detergents and of surfactants for detergents with the provisions of this Regulation and its Annexes.

Article 4

Limitations to the placing on the market

1. If a detergent contains surfactants for which the level of “ultimate aerobic biodegradation” is less than that stipulated in Annex III, manufacturers of detergents containing surfactants, and/or of surfactants for detergents may ask for derogation. Requests for derogation shall be made in accordance with the provisions of Articles 5 and 9.
2. The level of “primary biodegradability” shall be measured for all surfactants in detergents failing “ultimate aerobic biodegradation” tests. Detergent surfactants, for

which the level of “primary biodegradability” is less than that stipulated in Annex II, shall not be granted derogation.

Article 5

Granting of derogation

1. The request by a manufacturer for derogation shall be made by sending an application to the competent authorities of the Member State concerned, referred to in Article 8(1), and to the Commission, providing evidence relating to the criteria mentioned under Article 6(1).
2. Applications shall include a technical file supplying all the information and justifications necessary for evaluating the safety aspects related to the specific use of surfactants in detergents failing to comply with the biodegradability limits, as set out in Annexes II and III.

In addition to the results of tests stipulated in Annex III, the technical file shall include results of tests, as stipulated in Annexes II and IV.

3. The competent authorities of the Member States, receiving applications for derogation according to paragraphs 1 and 2 above, shall examine the requests, evaluate their compliance with the conditions for derogation and inform the Commission about the results without delay.

If the competent authority of the Member State deems it necessary, for the evaluation of the risk which may be caused by a substance and/or a preparation, it may ask for further information, verification and/or confirmatory tests concerning these substances and/or preparations or their transformation products, of which they have been notified or have received information under this Regulation.

4. The Commission may grant derogation in accordance with the procedure set out in Article 12(2). If necessary before granting derogation the Commission may evaluate further the matters indicated in paragraph 3 above.
5. Such derogations may allow, limit or severely restrict the placing on the market and the use of surfactants in detergents, depending on the results of the complementary risk assessment, as defined in Annex IV of this Regulation. They may include a phase-out period for placing on the market and the use of surfactants in detergents.
6. The Commission shall publish the list of surfactants that have obtained derogation, with the corresponding conditions or limitations of use, as provided in Annex V.

Article 6

Refusal of derogation

1. Where the Commission intends to refuse to grant a derogation it may do so on the basis of the following criteria:
 - use in high volumes;

- use in wide-dispersive applications, such as use by the general public, rather than in low-dispersive applications, such as specialized industrial and/or institutional cleaning;
 - socio-economic benefits do not outweigh the impact on human health and the environment.
2. As long as the Commission has not decided on a request for derogation, the use of the surfactant in question may be maintained, provided the manufacturer can show that the surfactant was already in use on the Community market at the date of entry into force of this Regulation and that the request for derogation was made within two years from that date. If the Commission refuses to grant a derogation for a surfactant, it may set a transitional period during which the use of the surfactant in question shall be phased-out. This transitional period shall not exceed two years.

Article 7

Testing of surfactants and listing of those that are banned or restricted for use

1. All tests referred to in Articles 3 and 4 and in Annexes II, III, IV and IX shall be conducted in compliance with the standard mentioned in Annex I.B.1. In cases where surfactants are used in detergents which were marketed before the entry into force of the above standard, existing tests that were performed using the best scientific knowledge available, and that were performed to a standard comparable to that of the standard mentioned in Annex I.B.1, may be accepted on a case-by-case basis. The manufacturer or the Member State may submit to the Commission any case over which there is doubt or dispute. A decision will then be taken in accordance with the procedure laid down in Article 12(2).
2. Surfactants, which are banned or restricted for use for not complying with this Regulation, are listed in Annex VI.
3. Surfactants listed in Annex VII are also banned or restricted for use in detergents, independently of the results of the tests under Annexes II, III, and IV, as a result of other Community legislation and in particular Directive 76/769/EEC.

Article 8

Duties of the Member States

1. Member States shall appoint the competent authority or authorities responsible for communicating and exchanging information relating to the management of this Regulation and inform the Commission of the name and full address of these authorities.
2. Each Member State shall notify the other Member States and the Commission the list of approved laboratories, with full name and address, that are competent and authorised to carry out the tests required by this Regulation and its Annexes. Member States shall demonstrate the competence of the above laboratories according to the standards mentioned in Annex I.B.
3. Where a Member State competent authority has grounds for believing that an approved laboratory does not possess the competence referred to in paragraph 2

above, it shall raise the matter in the Committee referred to in Article 12. If the Commission decides that the laboratory does not possess the required competence referred to in paragraph 2, the name of the approved laboratory shall be removed from the list referred to in paragraph 4. Article 15(2) shall apply.

4. The Commission shall publish the lists of competent authorities, mentioned in paragraph 1, and of approved laboratories, mentioned in paragraph 2, in the *Official Journal of the European Communities*.

Article 9

Duties of Manufacturers

1. Manufacturers placing on the market the preparations and/or the substances covered by this Regulation shall hold at the disposal of the competent authorities of the Member States:
 - information on one or more results of the tests mentioned in Annex III;
 - for those surfactants failing to pass tests stipulated in Annex III, and for which a request for derogation was made as referred to in Article 5:
 - i) a technical file on results of tests as stipulated in Annex II,
 - ii) a technical file on results of tests as stipulated in Annex IV.
2. Whenever substances and preparations covered by this Regulation are placed on the market, the manufacturer shall be responsible for the correct performance of the relevant tests mentioned above. He shall also have available - documentation on the testing carried out to demonstrate compliance with the Regulation, and to show that he is allowed to benefit from the property rights concerning the test results, other than for those test results already in the public domain.
3. Manufacturers placing on the market the preparations covered by this Regulation shall, upon request, make available without delay and free of charge, to any health care professional, a datasheet listing all ingredients as stipulated in *Annex VIII.C*.

Article 10

Control measures

1. Member State competent authorities may apply, as appropriate, control measures to detergents on the market by using the test and analytical methods referred to in Annex IX. These control measures shall not oblige manufacturers to repeat tests made by laboratories fulfilling the conditions indicated in Article 8(2), or to pay for any repeat or additional test, provided the initial test has shown compliance of detergents, or surfactants used in detergents, with this Regulation.
2. In cases of concern that the test-methods in Annex II, III, IV or IX have produced false positive results, the Member State competent authorities shall notify the Commission and the Commission may, in accordance with the procedure laid down in Article 12(2), verify those results and take the necessary measures.

Article 11
Labelling

1. The provisions of this Article are without prejudice to the provisions relating to the classification, packaging and labelling of dangerous substances and preparations in Directive 67/548/EEC and Directive 1999/45/EC on the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations .
2. The following information must appear in legible, visible and indelible characters on the packaging in which the detergents are put up for sale to the consumer:
 - a) the name of the product;
 - b) the name or trade name and address or trademark of the party responsible for placing the product on the market;
 - c) the address from which the datasheet referred to in Article 9(3) can be obtained.

The same information must appear on all documents accompanying detergents transported in bulk.

3. The packaging of detergents shall indicate the content, according to the specifications provided for in Annex VIII.A.
4. Additionally, the packaging of detergents sold to the general public intended to be used as laundry detergents shall bear the information provided for in Annex VIII.B.
5. In cases where a Member State has a national requirement to label in the national language(s), it shall notify the Commission thereof, and the manufacturer shall comply with that requirement for the information specified in paragraphs 3 and 4 above.

Article 12
Committee procedure

1. The Commission shall be assisted by a committee, composed of representatives of the Member States and chaired by the representative of the Commission.
2. Where reference is made to this paragraph, Articles 5 and 7 of Decision 1999/468/EC shall apply in compliance with Article 8 thereof.
3. The period provided for in Article 5(6) of Decision 1999/468/EC shall be three months.
4. The committee shall adopt its rules of procedure.

Article 13
Adaptation of the annexes

The amendments necessary for adapting Annexes I, II, III, IV, V, VI, VII, VIII and IX shall be adopted in accordance with the procedure laid down in Article 12(2), and shall, wherever possible, use European Standards.

Article 14
Free movement clause

Members States shall not prohibit, restrict or impede the placing on the market of detergents, and/or of surfactants for detergents, which comply with the requirements of this Regulation.

Article 15
Safeguard clause

1. Where a Member State has justifiable grounds for believing that a specific detergent, although satisfying the requirements of this Regulation, constitutes a risk to safety or health of humans or of animals or a risk to the environment, it may temporarily prohibit the placing on the market of that detergent in its territory or make it temporarily subject to special conditions.

It shall immediately inform the other Member States and the Commission thereof, giving the reasons for its decision.

2. After consultation of the Member States, or if appropriate of the relevant technical or scientific committee of the Commission, a decision shall be taken on the matter within ninety days in accordance with the procedure referred to in Article 12(2).

Article 16
Legislation to be replaced

1. The following Directives are hereby repealed with effect from the date of entry into force of this Regulation:
 - Directive 73/404/EEC;
 - Directive 73/405/EEC;
 - Directive 82/242/EEC;
 - Directive 82/243/EEC and
 - Directive 86/94/EEC.
2. References to the above Directives shall be construed as being references to the present Regulation.
3. Recommendation 89/542/EEC for the labelling of detergents falling under the scope of this Regulation is hereby repealed.

Article 17
Sanctions for non-compliance

1. No later than the day of the entry into force of this Regulation, Member States shall establish:
 - appropriate legal or administrative measures in order to deal with any non-compliance with the provisions of this Regulation and
 - dissuasive, effective and proportionate sanctions for any such non-compliance.
2. They shall immediately inform the Commission thereof.

Article 18
Entry into force

This Regulation shall enter into force 18 months after its publication in the *Official Journal of the European Communities*.

This Regulation shall be binding in its entirety and directly applicable in all Member States.

Done at,

For the European Parliament
The President

For the Council
The President

ANNEX I

A. List of products that are covered within the meaning of detergent

The following products containing soap or other surfactants are also covered within the meaning of the detergent definition as set out in Article 2(1):

- “Auxiliary washing preparation”, as intended for soaking (pre-washing), rinsing or bleaching clothes, household linen, etc.;
- “Laundry fabric-softener”, as intended to modify the feel of fabrics in processes which are to complement the washing of fabrics;
- “Cleaning preparation”, as intended for domestic all purposes cleaners and/or other water based cleaning of surfaces (e.g.: materials, products, machinery, mechanical appliances, means of transport and associated equipment, instruments, apparatus, etc.);
- “Other cleaning and washing preparations”, as intended for any other water-based processes.

B. Standards of accreditation concerning the laboratories that are competent and authorised to provide the necessary service for checking compliance of EC detergents with the requirements of this regulation and its annexes

1. Standards applicable at the level of the laboratories:

EN ISO/IEC 17025, General requirements for the competence of testing and calibration laboratories.

2. Standards applicable at the level of the accreditation bodies:

EN 45003, Calibration and testing laboratory accreditation system, general requirements for operation and recognition.

ANNEX II

“Primary biodegradability” test methods for surfactants in detergents

Primary biodegradability is measured by the determination in biodegraded liquors of the remaining level of parent surfactants. This *Annex* begins with a list of the test-methods common to all classes of surfactants, and then lists under headings A to D the analytical test procedures specific to each class of surfactant.

The pass criterion for primary biodegradability shall be a level of at least 80 %, as measured according to the tests below.

The reference method for the laboratory testing of surfactants in this Regulation is based on the “Confirmatory test procedure” in the OECD method, described in Annex IX.1. Changes to the Confirmatory test procedure are permissible provided that they comply with EN ISO 11733.

TEST METHODS

1. The OECD method published in the OECD's technical report of 11 June 1976 on the “Proposed Method for the Determination of the Biodegradability of Surfactants in Synthetic Detergents”.
2. The method in use in France, approved by the “arrêté du 24 décembre 1987” published in the *Journal officiel de la République française* of 30 December 1987, p. 15385, and by standard NF 73-260 of June 1981, published by the Association française de normalisation (AFNOR);
3. The method in use in Germany, established by the “Verordnung über die Abbaubarkeit anionischer und nichtionischer grenzflächenaktiver Stoffe in Wasch- und Reinigungsmitteln, of 30 January 1977, published in the *Bundesgesetzblatt*, Part I, p. 244, as set out in the Regulation amending that Regulation of 18 June 1980, published in the *Bundesgesetzblatt*, Part I, p. 706
4. The method in use in the United Kingdom called the “Porous Pot Test” and described in Technical Report No 70 (1978) of the Water Research Centre.
5. The “Confirmatory test procedure” in the OECD method, described in Annex IX.1 (including possible changes in operating conditions as proposed in EN ISO 11733). This is also the reference method used for the settlement of litigation.

A. Analytical Methods for Anionic Surfactants

The determination of anionic surfactants in the tests shall be done by the Methylene Blue Active Substance (MBAS) analysis according to the criteria established in Annex IX.2

For those anionic surfactants not reacting to the above-mentioned MBAS method, or if it seems more appropriate for reasons of efficiency or precision (this must be justified) appropriate instrumental analyses specific for the surfactant under study are to be applied. Samples of the pure surfactant of interest shall be provided by the manufacturer to the competent national authorities of the Member States upon request.

B. Analytical Methods for Non-ionic Surfactants

The determination of non-ionic surfactants in the tests shall be done by the Bismuth Active Substance (BiAS) method, according to the analytical procedure established in Annex IX.3.

For those non-ionic surfactants not reacting to the above-mentioned BiAS method, or if it seems more appropriate for reasons of efficiency or precision (this must be justified) appropriate instrumental analyses specific for the surfactant under study are to be applied. Samples of the pure surfactant of interest shall be provided by the manufacturer to the competent national authorities of the Member States upon request.

C. Analytical Methods for Cationic Surfactants

The determination of cationic surfactants in the tests shall be done by the Disulfine Blue Active Substance (DBAS) analysis according to the following DBAS procedures:

The method in use in the Federal Republic of Germany, (1989) DIN 38 409 – Ausgabe: 1989-07.

For those cationic surfactants not reacting to the above-mentioned test method, or if it seems more appropriate for reasons of efficiency or precision (this must be justified) appropriate instrumental analyses specific for the surfactant under study are to be applied. Samples of the pure surfactant of interest shall be provided by the manufacturer to the competent national authorities of the Member States upon request.

D. Analytical Methods for Amphoteric Surfactants

The determination of amphoteric surfactants in the tests shall be done by analysis following the procedures listed below:

1. *If cationics absent:*

The method in use in the Federal Republic of Germany, (1989) DIN 38 409-Teil 20.

2. *Otherwise:*

Orange II method (Boiteux, 1984).

For those amphoteric surfactants not reacting to the above-mentioned tests, or if it seems more appropriate for reasons of efficiency or precision (this must be justified) appropriate instrumental analyses specific for the surfactant under study are to be applied. Samples of the pure surfactant of interest shall be provided by the manufacturer to the competent authorities of the Member States upon request.

ANNEX III

“Ultimate biodegradability” (mineralisation) test methods for surfactants in detergents

A. The reference method for laboratory testing of surfactant ultimate biodegradability in this Regulation is based on the EN ISO Standard 14593: 1999 (CO₂ headspace test).

Surfactants in detergents shall be considered as biodegradable if the level of biodegradability (mineralisation) measured according to one of the five following tests²⁸ is at least 60 % within twenty-eight days:

1. EN ISO Standard 14593: 1999. Water quality. – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium. – Method by analysis of inorganic carbon in sealed vessels (CO₂ headspace test). Pre-adaptation is not to be used. The ten days window principle is not applied. (Reference method.)
2. Method Directive 67/548/EEC Annex V.C.4.C [Carbon dioxide (CO₂) Evolution Modified Sturm Test]: Pre-adaptation is not to be used. The ten days window principle is not applied.
3. Method Directive 67/548/EEC Annex V.C.4.E (Closed Bottle): Pre-adaptation is not to be used. The ten days window principle is not applied.
4. Method Directive 67/548/EEC Annex V.C.4.D (Manometric Respirometry): Pre-adaptation is not to be used. The ten days window principle is not applied.
5. Method Directive 67/548/EEC Annex V.C.4.F (MITI: Ministry of International Trade and Industry-Japan): Pre-adaptation is not to be used. The ten days window principle is not applied.

B. Depending on the physical characteristics of the surfactant, one of the methods listed below might be used if appropriately justified²⁹. It should be noted that the pass criterion of at least 70 % of these methods is to be considered as equivalent to the pass criterion of at least 60 % referred to in methods listed in point A above. The adequacy of the choice of the methods listed below shall be decided on a case by case confirmation, in accordance with Article 5 of this Regulation.

1. Method Directive 67/548/EEC Annex V.C.4.A (Dissolved Organic Carbon DOC Die-Away): Pre-adaptation is not to be used. The ten days window principle is not applied. The pass criteria for biodegradability measured according to the test shall be at least 70 % within twenty-eight days.
2. Method Directive 67/548/EEC Annex V.C.4.B (Modified OECD Screening-DOC Die-Away): Pre-adaptation is not to be used. The ten days window principle is not

²⁸ These five tests are identified as the most suitable for surfactants.

²⁹ The DOC methods could give results on the removal and not on the ultimate biodegradation. The Manometric Respirometry and the MITI would not be appropriate in some cases because the high initial test concentration could be inhibitory.

applied. The pass criteria for biodegradability measured according to the test shall be at least 70 % within twenty-eight days.

N.B. – All the above-mentioned methods from Council Directive 67/548/EEC can also be found in the publication *Classification, Packaging and Labelling of Dangerous Substances in the European Union*. Part 2: “Testing Methods”. European Commission 1997. ISBN 92-828-0076-8.

ANNEX IV

Complementary risk assessment for surfactants in detergents

For those surfactants for which environmental risk assessment is available in the context of Directive 93/67/EEC, or Regulation (EEC) No 793/93 and Regulation (EC) No 1488/94, and Technical Guidance Documents, this risk assessment shall be considered together with the complementary risk assessment run in the scope of this Regulation.

The complementary risk assessment run in the scope of this Regulation, in case it is likely that recalcitrant metabolites are produced, shall be considered in the context of assessments made on the basis of Directive 93/67/EEC and Regulation (EEC) No 793/93. This is to be assessed case by case and in particular on the basis of the results of the tests referred to in part 3 of this Annex.

The study shall cover the aquatic environmental compartment. Additional information relating to specific risk assessment concerns might be required by the Committee on a case by case basis. Additional information might include other environmental compartments such as sewage sludge and soil.

As noted in Articles 12(2) and 13 the guidelines included in this Annex for the Decisions on derogation may be adapted as appropriate on the basis of the accumulated experience.

The technical file referred to in Articles 5 and 9 shall contain at least the information described here below.

1. **Identity of the surfactant** (in accordance with the provisions laid down by Annex VII.A of Directive 67/548/EEC.)
 - 1.1. *Name*
 - 1.1.1. Names in the IUPAC nomenclature
 - 1.1.2. Other names
 - 1.1.3. CAS number and CAS name (if available)
 - 1.1.4. EINECS³⁰ or ELINCS³¹ numbers (if available)
 - 1.2. *Molecular and structural formula*
 - 1.3. *Composition of the surfactant*

³⁰ European Inventory of Existing Chemical Substances.

³¹ European List of Notified Chemical Substances.

2. **Information on the surfactant**

2.1. *Quantities of the surfactant used in detergents*

2.2. The information on use patterns given in this section shall be sufficient to allow an approximate but realistic estimate of function and environmental exposure to the surfactant as associated with its use in detergents. It shall include the following:

- importance of the application (societal value);
- use conditions (release scenario);
- use volume;
- availability and suitability of alternatives (performance and economic considerations);
- assessment of relevant environmental information.

3. **Information on the potential recalcitrant metabolite**

Toxicity information on test liquors shall be provided. If no data are available on residue identity, the information referred to in point 4.2.1 below may be requested, depending on the potential risk, the importance and the quantity of the surfactant used in detergents. In conflicting cases concerning this information, a Decision may be taken in accordance with Article 12(2).

4. **Additional studies**

4.1. *Biodegradability tests*

4.1.1. Pre-adapted inoculum

Any of the preferred tests described in Annex III, may be run with pre adapted inoculum in order to provide evidence of the relevance of pre-adaptation for the surfactant.

4.1.2. Inherent Biodegradability Tests

At least one of the tests referred to below shall be included:

- method Directive 67/548/EEC Annex V.C.12 (Modified SCAS test);
- method Directive 67/548/EEC Annex V.C.9 (Zahn-Wellens).

Failure to pass the inherent biodegradability test would indicate potential for persistency which may be considered, in general terms, as sufficient to prohibit the placing on the market of such a surfactant unless, as stated in Article 5, there are other justifiable reasons for granting a derogation.

4.1.3. Activated Sludge Simulation Biodegradability Tests

The following tests referred below shall be included:

- method Directive 67/548/EEC Annex V.C.10;

(including possible changes in operating conditions as proposed in EN ISO 11733).

Failure to pass the activated sludge simulation biodegradability test, would indicate potential for the release of the metabolites by sewage treatment, which may be considered, in general terms, as evidence of need for a more complete risk assessment.

4.2. Toxicity testing of biodegradation test liquors

Toxicity information on test liquors is to be provided on:

4.2.1. Chemical and physical information, such as:

- identity of the metabolite (and analytical means by which it was obtained);
- key physical chemical properties (water solubility, Octanol: Water partition coefficient (Log Po/w, etc.).

4.2.2. Effects on organisms

Fish: The test recommended is that in Annex V.C.1 of Directive 67/548/EEC

Daphnia: The test recommended is that in Annex V.C.2 of Directive 67/548/EEC

Algae: The test recommended is that in Annex V.C.3 of Directive 67/548/EEC

Bacteria: The test recommended is that in Annex V.C.11 of Directive 67/548/EEC

4.2.3. Degradation

Biotic: The test recommended is that in Annex V.C.5 of Directive 67/548/EEC

Abiotic: The test recommended is that in Annex V.C.7 of Directive 67/548/EEC. The information to be provided will consider as well the potential of metabolites for bio-concentration and their partitioning to the sediment phase.

Moreover, if some metabolites are suspected for endocrine disrupting activity, it is recommended to determine if these have potential to result in adverse effects as soon as validated testing schemes to assess such adverse effects are available.

N.B. – All the above mentioned methods from Directive 67/548/EEC can also be consulted in the publication *Classification, Packaging and Labelling of Dangerous Substances in the European Union*; Part 2: “Testing Methods”. European Commission 1997. ISBN 92-828-0076-8.

ANNEX V
List of surfactants that have obtained a derogation

The following detergent surfactants passing tests stipulated in Annex II, but not passing tests stipulated in Annex III, may be placed on the market by means of derogation stipulated in Article 5 and in accordance with the procedure laid down in Article 12(2) of this Regulation:

NAME in the IUPAC NOMENCLATURE	EINECS or ELINCS NUMBER	CAS NUMBER and CAS NAME	LIMITATIONS

EINECS means the European Inventory of Existing Commercial Substances. This inventory contains the definitive list of all substances deemed to be on the Community market on 18 September 1981.

ELINCS means the list of new substances as defined in Council Directive 92/32/EEC of 30 April 1992 amending for the seventh time Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances ³².

³² OJ L 154, 5.6.1992, p. 1.

ANNEX VI
List of banned or restricted detergent surfactants

The following detergent surfactants have been identified as not complying with the provisions of this Regulation:

NAME in the IUPAC NOMENCLATURE	EINECS or ELINCS NUMBER	CAS NUMBER and CAS NAME	LIMITATIONS

EINECS means the European Inventory of Existing Commercial Substances. This inventory contains the definitive list of all substances deemed to be on the Community market on 18 September 1981.

ELINCS means the list of new substances as defined in Directive 92/32/EEC.

ANNEX VII
List of banned or restricted detergent surfactants
in implementation of other community legislation

The following list of detergent surfactants incorporates surfactants covered by this Regulation and banned or restricted by other Community legislation, in particular Directive 76/769/EEC³³:

NAME in the IUPAC NOMENCLATURE	LEGISLATION ENFORCED	EINECS or ELINCS NUMBER	CAS NUMBER and CAS NAME	LIMITATIONS

EINECS means the European Inventory of Existing Commercial Substances. This inventory contains the definitive list of all substances deemed to be on the Community market on 18 September 1981.

ELINCS means the list of new substances as defined in Council Directive 92/32/EEC.

³³ It may refer as appropriate to the enforcement of International agreements and/or Organisations.

ANNEX VIII

Labelling and ingredient datasheet

A. Labelling for contents

As prescribed in Article 11(3) of this Regulation, the following provisions on labelling shall apply to the packaging of detergents sold to the general public.

The following weight percentage ranges:

- less than 5 %,
- 5 % or over but less than 15 %,
- 15 % or over but less than 30 %,
- 30 % and more,

shall be used to indicate the content of the constituents listed below where they are added in a concentration above 0,2 weight %:

- phosphates,
- phosphonates,
- anionic surfactants,
- cationic surfactants,
- amphoteric surfactants,
- non-ionic surfactants,
- oxygen-based bleaching agents,
- chlorine-based bleaching agents,
- EDTA,
- nitrilotriacetic acid,
- phenols and halogenated phenols,
- paradichlorobenzene,
- aromatic hydrocarbons,
- aliphatic hydrocarbons,
- halogenated hydrocarbons,
- soap,

- zeolites,
- polycarboxylates.

For other constituents, if added, neither the above percentage ranges nor the concentration threshold of 0,2 % shall be applied. The following classes of constituent, if added, shall be listed irrespective of their concentration:

- enzymes,
- disinfectants.

If added, preservation agents shall be listed, irrespective of their concentration, using where possible the common nomenclature established under Article 8 of Directive 76/768/EEC.

If added, fragrances that appear on the list of allergenic perfume ingredients, first established by the Scientific Committee on Cosmetics and Non Food Products in its opinion SCCNFP/0017/98³⁴, shall be listed using the nomenclature established by that Committee, irrespective of their concentration.

For detergents intended to be used in the industrial sector, and not made available to members of the general public, the above-mentioned requirements do not have to be fulfilled if the equivalent information is provided by means of technical data sheets, safety data sheets, or in a similar appropriate manner.

B. Labelling for Dosage information

As prescribed in Article 11(4) of this Regulation, the following provisions on labelling shall apply to the packaging of detergents sold to the general public. The packaging of detergents sold to the general public intended to be used as laundry detergents shall bear the following information:

- The recommended quantities and/or dosage instructions expressed in millilitres or grams appropriate to a standard washing machine load, for specified water hardness classes and making provision for one or two cycle washing processes.
- The number of standard washing machine loads of ‘normally soiled’ fabrics that can be washed with the contents of the package using water of medium hardness, corresponding to 2,5 millimoles CaCO₃/l.
- The capacity of any measuring cup, if provided, shall be indicated in millilitres or grams.

The standard washing machine loads are 4,5 kg dry fabric for heavy-duty detergents and 2,5 kg dry fabric for low-duty detergents in line with the definitions of Commission Decision 1999/476/EC establishing the ecological criteria for the award of the Community eco-label to laundry detergents. A detergent shall be considered to be a heavy-duty detergent unless the claims of the manufacturer or importer predominantly promotes fabric care *i.e.* low temperature wash, delicate fibres and colours.

³⁴ http://europa.eu.int/comm/food/fs/sc/sccp/out98_en.html

C. Ingredient datasheet

The following provisions shall apply to the listing of ingredients on the datasheet referred to in Article 9(3) of this Regulation.

The datasheet shall list the name of the detergent and of the manufacturer.

All ingredients shall be listed; they shall be listed in order of decreasing abundance by weight, and the list shall be sub-divided into the following weight percentage ranges:

- 10 % or more,
- 1 % or over, but less than 10 %,
- 0,1 % or over, but less than 1 %,
- less than 0,1 %.

Impurities shall not be considered to be ingredients.

The common chemical name or IUPAC³⁵ name, the CAS number, and, where available, the INCI³⁶ name, and the European Pharmacopoeia name, shall be given for each ingredient.

³⁵ International Union of Pure and Applied Chemistry
³⁶ International Nomenclature Cosmetic Ingredient

ANNEX IX

Test methods and analytical methods

The following test and analytical methods apply to control procedures of detergents on the market made by Member States:

1. REFERENCE METHOD (confirmatory test)

1.1. Definition

This method describes a laboratory model of the activated sludge + secondary settler which is designed to simulate municipal sewage treatment. The conditions described are those from Directives that preceded this Regulation. Improved state-of-the-art operating conditions can be applied to this test method as described in EN ISO 11733

1.2. Equipment needed for measurement

The method of measurement employs the small-activated sludge plant shown in Figure 1, and in greater detail in Figure 2. The equipment consists of a sewage vessel A for synthetic sewage, dosing pump B, aeration vessel C, settling vessel D, air-lift pump E to recycle the activated sludge, and vessel F for collecting the treated effluent.

Vessels A and F must be of glass or suitable plastic and hold at least twenty-four litres. Pump B must provide a constant flow of synthetic sewage to the aeration vessel; this vessel, during normal operation, contains three litres of mixed liquor. A sintered aeration cube G is suspended in the vessel C at the apex of the cone. The quantity of air blown through the aerator shall be monitored by means of a flow meter H.

1.3. Synthetic sewage

A synthetic sewage is employed for the test. Dissolve in each litre of tap water:

- 160 mg peptone;
- 110 mg meat extract;
- 30 mg urea, $\text{CO}(\text{NH}_2)_2$;
- 7 mg sodium chloride, NaCl ;
- 4 mg calcium chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$;
- 2 mg magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$;
- 28 mg of di-potassium hydrogen phosphate, K_2HPO_4 ;
- and 10 ± 1 mg of the surfactant.

The synthetic sewage is freshly prepared daily.

1.4. Preparation of samples

Uncompounded surfactants are examined in the original state. Active content of surfactant samples must be determined in order to prepare the synthetic sewage (1.3).

1.5. Operation of equipment

Initially, fill aeration vessel C and settling vessel D with synthetic sewage. The height of the vessel D should be so fixed that the volume contained in the aeration vessel C is three litres. Inoculation is made by introducing 3 ml of a secondary effluent of good quality, freshly collected from a treatment plant dealing with a predominantly domestic sewage. The effluent must be kept under aerobic conditions in the period between sampling and application. Then set the aerator G, air-lift E and dosing device B in operation. The synthetic sewage must pass through the aeration vessel C at a rate of one litre per hour; this gives a mean retention time of three hours.

The rate of aeration should be so regulated that the contents of vessel C are kept constantly in suspension and the dissolved oxygen content is at least 2 mg/l. Foaming must be prevented by appropriate means. Anti-foaming agents that inhibit the activated sludge or contain surfactants must not be used. The air-lift pump E must be set so that the activated sludge from the settling vessel is continually and regularly recycled to aeration vessel C. Sludge which has accumulated around the top of the aeration vessel C, in the base of the settling vessel D, or in the circulation circuit must be returned to the circulation at least once each day by brushing or some other appropriate means. When the sludge fails to settle, its settleability may be increased by the addition of 2 ml portions of a 5 % solution of ferric chloride, repeated as necessary.

The effluent from the settling vessel D is accumulated in vessel F for twenty-four hours, following which a sample is taken after thorough mixing. Vessel F must then be carefully cleaned.

1.6. Checking measuring equipment

The surfactant content (in mg/l) of the synthetic sewage is determined immediately before use.

The surfactant content (in mg/l) of the effluent collected over twenty-four hours in vessel F should be determined analytically by the same method, immediately after collection: otherwise the samples must be preserved, preferably by freezing. The concentrations must be determined to the nearest 0,1 mg/l surfactant

As a check on the efficiency of the process, the chemical oxygen demand (COD) or the dissolved organic carbon (DOC) of the glass fibre filtered effluent accumulated in vessel F and of the filtered synthetic sewage in vessel A is measured at least twice per week.

The reduction in COD or DOC should level off when a roughly regular daily surfactant degradation is obtained at the end of the running-in period shown in Figure 3.

The content of dry matter in the activated sludge contained in the aeration vessel should be determined twice a week in g/l. If it is more than 2,5 g/l, the excess activated sludge must be discarded.

The degradation test is performed at room temperature; this should be steady and kept between 19-24 °C.

1.7. Calculation of biodegradability

The percentage degradation of surfactant must be calculated every day on the basis of the surfactant content in mg/l of the synthetic sewage and of the corresponding effluent accumulated in vessel F.

The degradability values thus obtained should be presented graphically as in Figure 3.

The degradability of the surfactant should be calculated as the arithmetic mean of the values obtained over the twenty-one days that follow the running-in and acclimatisation period, during which degradation has been regular and the operation of the plant trouble-free. In any event the duration of the running-in period should not exceed six weeks.

The daily degradation values are calculated to the nearest 0,1 % but the final result is given to the nearest whole number.

In some cases it may be permissible to reduce the frequency of sampling but at least fourteen results collected over the twenty-one days which follow the running-in period should be used in calculating the average.

2. DETERMINATION OF ANIONIC SURFACTANTS IN BIODEGRADABILITY TESTS

2.1. Principle

The method is based on the fact that the cationic dye methylene blue forms blue salts with anionic surfactants [MBAS³⁷], which can be extracted with chloroform. To eliminate interference, the extraction is first effected from alkaline solution and the extract is then shaken with acidic methylene blue solution. The absorbency of the separated organic phase is measured photometrically at the wavelength of maximum absorption of 650 nm.

2.2. Reagents and equipment

2.2.1. Buffer solution pH 10

Dissolve 24 g sodium bicarbonate, NaHCO₃ AR, and 27 g anhydrous sodium carbonate (Na₂CO₃) AR in deionised water and dilute to 1 000 ml.

2.2.2. Neutral methylene blue solution

Dissolve 0,35 g methylene blue AR in deionised water and dilute to 1 000 ml. Prepare the solution at least twenty-four hours before use. The absorbency of the blank chloroform phase, measured against chloroform must not exceed 0,015 per 1 cm of layer thickness at 650 nm.

2.2.3. Acidic methylene blue solution

Dissolve 0,35 g methylene blue AR in 500 ml deionised water and mix with 6,5 ml H₂SO₄ (d = 1,84 g/ml). Dilute to 1 000 ml with deionised water. Prepare the solution at least twenty-

³⁷ MBAS means Methylene Blue Active Substances.

four hours before use. The absorbency of the blank chloroform phase, measured against chloroform must not exceed 0,015 per 1 cm of layer thickness at 650 nm.

2.2.4. *Chloroform (trichloromethane) AR freshly distilled*

2.2.5. *Dodecyl benzene sulphonic acid methyl ester*

2.2.6. *Ethanolic potassium hydroxide solution, KOH 0,1 M*

2.2.7. *Ethanol pure, C₂H₅OH*

2.2.8. *Sulphuric acid, H₂SO₄ 0,5 M*

2.2.9. *Phenolphthalein solution*

Dissolve 1 g phenolphthalein in 50 ml ethanol and add 50 ml deionised water while stirring continuously. Filter off any precipitate obtained.

2.2.10. *Methanolic hydrochloric acid: 250 ml hydrochloric acid AR and 750 ml methanol*

2.2.11. *Separating funnel, 250 ml*

2.2.12. *Graduated flask, 50 ml*

2.2.13. *Graduated flask, 500 ml*

2.2.14. *Graduated flask, 1 000 ml*

2.2.15. *Round-bottomed flask with ground glass stopper and reflux condenser, 250 ml; boiling granules*

2.2.16. *pH meter*

2.2.17. *Photometer for measurements at 650 nm, with 1 to 5 cm cells*

2.2.18. *Qualitative grade filter paper*

2.3. Procedure

The samples for analysis must not be taken through a layer of foam.

After thorough cleaning with water, the equipment used for the analysis must be thoroughly rinsed with methanolic hydrochloric acid (2.2.10) and then with deionised water before using.

Filter the activated sludge plant influent and effluent to be examined immediately on sampling. Discard the first 100 ml of the filtrates.

Place a measured volume of the sample, neutralised if necessary, into a 250 ml separating funnel (2.2.11). The volume of sample should contain between 20 and 150 µg of MBAS. At the lower MBAS content, up to 100 ml of sample may be used. When using less than 100 ml, dilute to 100 ml with deionised water. Add to the sample 10 ml of buffer solution (2.2.1), 5 ml of neutral methylene blue solution (2.2.2) and 15 ml of chloroform (2.2.4). Shake the mixture uniformly and not too vigorously for one minute. After phase separation, run the chloroform layer into a second separating funnel, containing 110 ml of deionised water and 5 ml of acidic

methylene blue solution (2.2.3). Shake the mixture for one minute. Pass the chloroform layer through a cotton-wool filter previously cleaned and wetted with chloroform into a graduated flask (2.2.12).

Extract the alkaline and acid solutions three times, using 10 ml of chloroform for the second and third extractions. Filter the combined chloroform extracts through the same cotton wool filter and dilute to the mark in the 50 ml flask (2.2.12) with chloroform used for rewashing the cotton wool. Measure the absorbency of the chloroform solution with a photometer at 650 nm in 1 to 5 cm cells against chloroform. Run a blank determination through the whole procedure.

2.4. Calibration curve

Prepare a calibration solution from the standard substance dodecylbenzene sulphonic acid methyl ester (tetrapropylene type mol. wt. 340) after saponification into the potassium salt. The MBAS is calculated as sodium dodecyl benzene sulphonate (mol. wt. 348).

From a weighing pipette, weigh 400 to 450 mg of dodecyl-benzene-sulphonic-acid-methyl-ester (2.2.5) to the nearest 0,1 mg in a round-bottomed flask and add 50 ml of ethanolic potassium hydroxide solution (2.2.6) and some boiling granules. After mounting the reflux condenser, boil for one hour. After cooling, wash the condenser and ground glass joint with about 30 ml of ethanol, and add these washings to the contents of the flask. Titrate the solution with sulphuric acid against phenolphthalein until it becomes colourless. Transfer this solution to a 1 000 ml graduated flask (2.2.14), dilute to the mark with deionised water and mix.

Part of this surfactant stock solution is then further diluted. Withdraw 25 ml, transfer to a 500 ml graduated flask (2.2.13), dilute to the mark with deionised water and mix.

This standard solution contains:

$$\frac{E \times 1,023}{20\,000} \text{ mg MBAS per ml,}$$

where E is the sample weight in mg.

To establish the calibration curve, withdraw 1, 2, 4, 6, 8 ml portions of the standard solution and dilute each to 100 ml with deionised water. Then proceed as stated under item 2.3 including a blank determination.

2.5. Calculation of results

The amount of anionic surfactant (MBAS) in the sample is read from the calibration curve (2.4). The MBAS content of the sample is given by:

$$\frac{\text{mg MBAS} \times 1\,000}{V} = \text{MBAS mg/l}$$

where: V = ml volume of the sample used.

Express the results as sodium dodecylbenzene sulphonate (MW 348).

2.6. Expression of results

Express the results as MBAS mg/l to the nearest 0,1.

3. DETERMINATION OF NON-IONIC SURFACTANTS IN BIODEGRADATION TEST LIQUORS

3.1 Principle

Surface active agents are concentrated and isolated by gas stripping. In the sample used, the quantity of non-ionic surfactant should be in the range 250-800 µg.

The stripped surfactant is dissolved in ethyl acetate.

After phase separation and evaporation of the solvent, the non-ionic surfactant is precipitated in aqueous solution with modified Dragendorff reagent ($\text{KBiI}_4 + \text{BaCl}_2 + \text{glacial acetic acid}$).

The precipitate is filtered, washed with glacial acetic acid and dissolved in ammonium tartrate solution. The bismuth in the solution is titrated potentiometrically with pyrrolidinedithiocarbamate solution at pH 4-5 using a bright platinum indicator electrode and a calomel or silver/silver chloride reference electrode. The method is applicable to non-ionic surfactants containing 6-30 alkylene oxide groups.

The titration result is multiplied by the empirical factor of 54 for conversion to the reference substance nonylphenol condensed with 10 mols ethylene oxide (NP 10).

3.2. Reagents and Equipment

Reagents are to be made up in deionised water.

3.2.1. *Pure ethyl acetate, freshly distilled*

3.2.2. *Sodium bicarbonate, NaHCO_3 AR*

3.2.3. *Dilute hydrochloric acid [20 ml concentrated acid (HCl) diluted to 1 000 ml with water]*

3.2.4. *Methanol AR, freshly distilled, stored in a glass bottle.*

3.2.5. *Bromocresol purple, 0,1 g in 100 ml methanol.*

3.2.6. *Precipitating agent: the precipitating agent is a mixture of two volumes of solution A and one volume of solution B. The mixture is stored in a brown bottle and can be used for up to one week after mixing.*

3.2.6.1. Solution A

Dissolve 1,7 g bismuth nitrate, $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ AR, in 20 ml glacial acetic acid, and make up to 100 ml with water. Then dissolve 65 g potassium iodide AR in 200 ml water. Mix these two solutions in a 1 000 ml measuring flask, add 200 ml glacial acetic acid (3.2.7) and make up to 1 000 ml with water.

3.2.6.2. Solution B

Dissolve 290 g barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ AR, in 1 000 ml of water.

3.2.7. *Glacial acetic acid 99-100 % (lower concentrations are unsuitable).*

3.2.8. *Ammonium tartrate solution: mix 12,4 g tartaric acid AR and 12,4 ml of ammonia solution AR ($d = 0,910$ g/ml) and make up to 1 000 ml with water (or use the equivalent amount of ammonium tartrate AR).*

3.2.9. *Dilute ammonia solution: 40 ml ammonia solution AR ($d = 0,910$ g/ml) diluted to 1 000 ml with water.*

3.2.10. *Standard acetate buffer: dissolve 40 g solid sodium hydroxide AR, in 500 ml water in a beaker and allow to cool. Add 120 ml glacial acetic acid (3.2.7). Mix thoroughly, cool and transfer to a 1 000 ml volumetric flask. Make up to the mark with water.*

3.2.11. *Pyrrolidinedithiocarbamate solution (known as "carbate solution"): dissolve 103 mg sodium pyrrolidinedithiocarbamate, $\text{C}_5\text{H}_8\text{NNaS}_2 \cdot 2\text{H}_2\text{O}$, in about 500 ml water, add 10 ml of *n*-amyl alcohol AR and 0,5 g NaHCO_3 AR, and make up to 1 000 ml with water.*

3.2.12. *Copper sulphate solution (for standardisation of 3.2.11).*

STOCK SOLUTION

Mix 1 249 g copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ AR, with 50 ml 0,5 M sulphuric acid and make up to 1 000 ml with water.

STANDARD SOLUTION

Mix 50 ml stock solution with 10 ml 0,5 M H_2SO_4 and make up to 1 000 ml with water.

3.2.13. *Sodium chloride AR*

3.2.14. *Gas-stripping apparatus (see Figure 5).*

The diameter of the sintered disc must be the same as the internal diameter of the cylinder.

3.2.15. *Separating funnel, 250 ml.*

3.2.16. *Magnetic stirrer with magnet 25-30 mm.*

3.2.17. *Gooch crucible, diameter of the perforated base = 25 mm, Type G4.*

3.2.18. *Circular glass-fibre filter papers, 27 mm diameter with fibre diameter 0,3-1,5 μm .*

3.2.19. *Two filter flasks with adapters and rubber collars, 500 and 250 ml respectively.*

3.2.20. *Recording potentiometer fitted with a bright platinum indicator electrode and a calomel or silver/silver chloride reference electrode with a 250 mV range, with automatic burette of 20-25 ml capacity, or alternative manual equipment.*

3.3. Method

3.3.1. Concentration and separation of the surfactant

Filter the aqueous sample through a qualitative filter paper. Discard the first 100 ml of the filtrate.

Into the stripping apparatus, previously rinsed with ethyl acetate, place a measured quantity of the sample, such that it contains between 250-800 µg non-ionic surfactant.

To improve the separation add 100 g sodium chloride and 5 g sodium bicarbonate.

If the volume of the sample exceeds 500 ml, add these salts to the stripping apparatus in solid form, and dissolve by passing nitrogen or air through.

If a smaller-sized sample is used, dissolve the salts in 400 ml water and then add to the stripping apparatus.

Add water to bring the level to the upper stopcock.

Cautiously add 100 ml ethyl acetate on top of the mater.

Fill the wash-bottle in the gas-line (nitrogen or air) two-thirds full with ethyl acetate.

Pass a gas stream of 30-60 l/h through the apparatus; the use of a flowmeter is recommended. The rate of aeration must be increased gradually at the beginning. The gas rate must be so adjusted that the phases remain noticeably separate to minimise the mixing of the phases and the solution of the ethyl acetate in the water. Stop the gas flow after five minutes.

If there is a reduction of more than 20 % in the volume of the organic phase through solution in water, the sublation must be repeated paying special attention to the rate of gas flow.

Run off the organic phase into a separating funnel. Return any water in the separating funnel from the aqueous phase - it should only be a few ml - to the stripping apparatus. Filter the ethyl acetate phase through a dry qualitative filter paper into a 250 ml beaker.

Put a further 100 ml ethyl acetate into the stripping apparatus and again pass nitrogen or air through for five minutes. Draw off the organic phase into the separating funnel used for the first separation, reject the aqueous phase and run the organic phase through the same filter as the first ethyl acetate portion. Rinse both the separating funnel and the filter with about 20 ml ethyl acetate.

Evaporate the ethyl acetate extract to dryness using a water-bath (fume cupboard). Direct a gentle stream of air over the surface of the solution to accelerate the evaporation.

3.3.2. Precipitation and filtration

Dissolve the dry residue from 3.3.1 in 5 ml methanol, add 40 ml water and 0,5 ml dilute HCl (3.2.3) and stir the mixture with a magnetic stirrer.

To this solution add 30 ml of precipitating agent (3.2.6) from a measuring cylinder. The precipitate forms after repeated stirring. After stirring for ten minutes leave the mixture to stand for at least five minutes.

Filter the mixture through a Gooch crucible, the base of which is covered with a glass-fibre filter paper. First wash the filter under suction with about 2 ml glacial acetic acid. Then thoroughly wash the beaker, magnet, and crucible with glacial acetic acid, of which about 40-50 ml is necessary. It is not necessary to quantitatively transfer the precipitate adhering to the sides of the beaker, to the filter, because the solution of the precipitate for the titration is returned to the precipitating beaker, and the remaining precipitate will then be dissolved.

3.3.3. *Dissolution of the precipitate*

Dissolve the precipitate in the filter crucible by the addition of hot ammonium tartrate solution (about 80 °C) (3.2.8) in three portions of 10 ml each. Allow each portion to stand in the crucible for some minutes before being sucked through the filter into the flask.

Put the contents of the filter flask into the beaker used for the precipitation. Rinse the sides of the beaker with a further 20 ml of tartrate solution to dissolve the rest of the precipitate.

Carefully wash the crucible, adapter and filter flask with 150-200 ml water, and return the rinsing water to the beaker used for the precipitation.

3.3.4. *The titration*

Stir the solution using a magnetic stirrer (3.2.16), add a few drops of bromocresol purple (3.2.5) and add the dilute ammonia solution (3.2.9) until the colour turns violet (the solution is initially weakly acid from the residue of acetic acid used for rinsing).

Then add 10 ml standard acetate buffer (3.2.10), immerse the electrodes in the solution, and titrate potentiometrically with standard "carbate solution" (3.2.11), the burette tip being immersed in the solution.

The titration rate should not exceed 2 ml/min.

The endpoint is the intersection of the tangents to the two branches of the potential curve. It will be observed occasionally that the inflection in the potential curve becomes flattened; this can be eliminated by carefully cleaning the platinum electrode (by polishing with emery paper).

3.3.5. *Blank determinations*

At the same time run a blank determination through the whole procedure with 5 ml methanol and 40 ml water, according to the instructions in 3.3.2. The blank titration should be below 1 ml, otherwise the purity of the reagents (3.2.3, 3.2.7, 3.2.8, 3.2.9, 3.2.10) is suspect, especially their content of heavy metals, and they must be replaced. The blank must be taken into account in the calculation of the results.

3.3.6. *Control of the factor of the "carbate solution"*

Determine the factor for the carbate solution on the day of use. To do this, titrate 10 ml of the copper sulphate solution (3.2.12) with "carbate solution" after the addition of 100 ml water and 10 ml standard acetate buffer (3.2.10). If the amount used is a ml, the factor f is:

$$f = \frac{10}{a}$$

and all the results of the titration are multiplied by this factor.

3.4. Calculation of results

Every non-ionic surfactant has its own factor, depending on its composition, particularly on the length of the alkene oxide chain. The concentration of non-ionic surfactant is expressed in relation to a standard substance – a nonyl phenol with ten ethylene oxide units (NP 10) – for which the conversion factor is 0,054.

Using this factor the amount of surfactant present in the sample is found expressed as mg of NP 10 equivalent, as follows:

$$(b - c).f.0,054 = \text{mg non-ionic surfactant as NP 10}$$

where:

b = volume of “carbate solution” used by the sample (ml),

c = volume of “carbate solution” used by the blank (ml),

f = factor of the ”carbate solution”.

3.5 Expression of results

Express the results in mg/l as NP 10 to the nearest 0,1.

4. PRELIMINARY TREATMENT OF ANIONIC SURFACTANTS TO BE TESTED

4.1. Preliminary notes

4.1.1. Treatment of samples

The treatment of anionic surface-active agents and formulated detergents prior to the determination of primary biodegradability in the confirmatory test is:

PRODUCTS	TREATMENT
Anionic surfactants	None
Formulated detergents	Alcoholic extraction followed by separation of the anionic surfactants by ion exchange

The purpose of the alcoholic extraction is to eliminate the insoluble and inorganic ingredients of the commercial product, which in some circumstances might upset the biodegradability test.

4.1.2. Ion-exchange procedure

Isolation and separation of anionic surface active agents from soap, non-ionic and cationic surfactants are required for correct biodegradability tests.

This is achieved by an ion-exchange technique using a macro-porous exchange resin and suitable eluants for fractional elution. Thus soap, anionic and non-ionic surfactants may be isolated in one procedure.

4.1.3. Analytical control

After homogenising, the concentration of anionic surfactants in the synthetic detergent is determined according to the MBAS analytical procedure. The soap content is determined by a suitable analytical method. This analysis of the products is necessary to calculate the quantities required for preparing fractions for the biodegradability test.

Quantitative extraction is not necessary; however, at least 80 % of the anionic surfactants should be extracted. Usually, 90 % or more is obtained.

4.2. Principle

From a homogeneous sample (powders, dried pastes and dried liquids) an ethanol extract is obtained which contains the surfactants, soap and other alcohol-soluble constituents of the synthetic detergent sample.

The ethanol extract is evaporated to dryness, dissolved in an isopropanol/water mixture and the solution obtained is passed through a strongly acidic cation exchange/macro-porous anion exchange combination heated to 50 °C. This temperature is necessary to prevent the precipitation of any fatty acids which may be present in acidic media.

Any non-ionic surfactants remain in the effluent.

Soap fatty acids are separated by extraction with ethanol containing CO₂. The anionic surfactants are then obtained as ammonium salts, by elution with an aqueous isopropanolic solution of ammonium bicarbonate. These ammonium salts are used for the degradation test.

Cationic surfactants that might upset the biodegradability test and the analytical procedure are eliminated by the cation exchanger placed above the anion exchanger.

4.3. Chemicals and equipment

4.3.1. *Deionised water*

4.3.2. *Ethanol, 95 % (v/v) C₂H₅OH (permissible denaturant: methyl ethyl ketone or methanol)*

4.3.3. *Isopropanol/water mixture (50/50 v/v):*

- 50 parts by volume isopropanol, CH₃CHOH.CH₃, and
- 50 parts by volume water (4.3.1)

4.3.4. *Solution of carbon dioxide in ethanol (approximately 0,1 % CO₂): using a delivery tube with a built-in sinter, pass carbon dioxide, CO₂, through the ethanol (4.3.2) for ten minutes . Use fresh solutions only*

4.3.5. *Ammonium bicarbonate solution (60/40 v/v): 0,3 mol NH₄HCO₃ in 1 000 ml of an isopropanol/water mixture consisting of 60 parts by volume isopropanol and 40 parts by volume water (4.3.1)*

4.3.6. *Cation exchanger (KAT), strongly acidic, resistant to alcohol (50-100 mesh)*

- 4.3.7. *Anion exchanger (AAT), macro-porous, Merck Lewatit MP 7080 (70-150 mesh) or equivalent*
- 4.3.8. *Hydrochloric acid, 10 % HCl (w/w)*
- 4.3.9. *2 000 ml round-bottomed flask with ground glass stopper and reflux condenser*
- 4.3.10. *90 mm diameter suction filter (heatable) for filter papers*
- 4.3.11. *2 000 ml filter flask*
- 4.3.12. *Exchange columns with heating jacket and tap: inner tube 60 mm in diameter and 450 mm in height (see Figure 4)*
- 4.3.13. *Water-bath*
- 4.3.14. *Vacuum drying oven*
- 4.3.15. *Thermostat*
- 4.3.16. *Rotary evaporator*

4.4. Preparation of extract and separation of anionic active agents

4.4.1. Preparation of extract

The quantity of surfactants necessary for the biodegradation test is about 50 g MBAS.

Normally, the quantity of product to be extracted will not exceed 1 000 g, but it may be necessary to extract further quantities of sample. For practical reasons, the quantity of product used should in most cases be limited to 5 000 g in preparing extracts for the biodegradation test.

Experience has shown that there are advantages in using a number of small extractions rather than one large extraction. The exchanger quantities specified are designed for a working capacity of 600-700 mmoles of surfactants and soap.

4.4.2. Isolation of alcohol-soluble constituents

Add 250 g of the synthetic detergent to be analysed to 1 250 ml ethanol, heat the mixture to boiling point and reflux for one hour with stirring. Pass the hot alcoholic solution through a coarse-pored suction filter heated to 50 °C and filter rapidly. Wash the flask and suction filter with approximately 200 ml hot ethanol. Collect the filtrate and filter washings in a filter flask.

In the case of pastes or liquid products to be analysed, make sure that not more than 55 g anionic surfactants and 35 g soap are contained in the sample. Evaporate this weighed sample to dryness. Dissolve the residue in 2000 ml ethanol and proceed as described above.

In the case of powders of low apparent density (< 300 g/l) it is recommended to increase the ethanol ratio in the relation 20:1. Evaporate the ethanolic filtrate to dryness, preferably by means of a rotary evaporator. Repeat the operation if a greater quantity of extract is required. Dissolve the residue in 5 000 ml isopropanol/water mixture.

4.4.3. Preparation of ion-exchange columns

CATION-EXCHANGE COLUMN

Place 600 ml cation-exchange resin (4.3.6) in a 3 000 ml beaker and cover by adding 2 000 ml hydrochloric acid (4.3.8). Allow standing for at least two hours, with occasional stirring. Decant the acid and transfer the resin into the column (4.3.12) by means of deionised water. The column should contain a glass-wool plug. Wash the column with deionised water at a rate of 10-30 ml/min until the eluate is free of chloride. Displace the water with 2 000 ml isopropanol/water mixture (4.3.3) at a rate of 10-30 ml/min. The exchange column is now ready for operation.

ANION-EXCHANGE COLUMN

Place 600 ml anion-exchange resin (4.3.7) in a 3 000 ml beaker and cover by adding 2 000 ml deionised water. Allow the resin to swell for at least two hours. Transfer the resin into the column by means of deionised water. The column should contain a glass-wool plug.

Wash the column with 0,3 M ammonium bicarbonate solution (4.3.5) until free of chloride. This requires about 5 000 ml solution. Wash again with 2 000 ml deionised water. Displace the water with 2 000 ml isopropanol/water mixture (4.3.3) at a rate of 10-30 ml/min. The exchange column is now in the OH-form and ready for operation.

4.4.4. Ion-exchange procedure

Connect the exchange columns so that the cation-exchange column is placed on top of the anion-exchange column. Heat the exchange columns to 50 °C using thermostatic control. Heat 5 000 ml of the solution obtained in item 4.4.2 to 60 °C and pass the solution through the exchanger combination at a rate of 20 ml/min. Wash the columns with 1 000 ml hot isopropanol/water mixture (4.3.3).

To obtain the anionic surface active agents (MBAS), disconnect the KAT column. Using 5 000 ml ethanol/CO₂ solution at 50 °C (4.3.4), elute the soap fatty acids out of the KAT column. Reject the eluate.

Then elute the MBAS out of the AAT column with 5 000 ml ammonium bicarbonate solution (4.3.5). Evaporate the eluate to dryness using a steam bath or in a rotary evaporator. The residue contains the MBAS (as ammonium salt) and possible non-surfactant anionics that have no detrimental effect on the biodegradation test. Add deionised water to the residue until a definite volume is obtained and determine the MBAS content in an aliquot. The solution is used as a standard solution of the anionic synthetic detergents for the biodegradation test. The solution should be kept at a temperature below 5 °C.

4.4.5. Regeneration of ion exchange resins

The cation exchanger is rejected after use.

Passing an additional quantity of ammonium bicarbonate solution (4.3.5) down the column at a flow rate of approximately 10 ml/min until the eluate is free from anionic surfactants (methylene blue test) regenerates the anion-exchange resin. Then pass 2 000 ml isopropanol/water mixture (4.3.3) down the anion exchanger to wash. The anion exchanger is again ready for operation.

5. PRELIMINARY TREATMENT OF NON-IONIC SURFACTANTS TO BE TESTED

5.1. Preliminary notes

5.1.1 Treatment of samples

The treatment of non-ionic surface-active agents and formulated detergents prior to the determination of primary biodegradability in the confirmatory test is:

PRODUCTS	TREATMENT
Non-ionic surfactants	None
Formulated detergents	Alcoholic extraction followed by separation of the non-ionic surfactants by ion exchange

The purpose of the alcoholic extraction is to eliminate the insoluble and inorganic ingredients of the commercial product, which in some circumstances might upset the biodegradability test

5.1.2 Ion-exchange procedure

Isolation and separation of non-ionic surface active agents from soap, anionic and cationic surfactants are required for correct biodegradability tests.

This is achieved by an ion exchange technique using a macro-porous exchange resin and suitable eluants for fractional elution. Thus soap, anionic and non-ionic surfactants may be isolated in one procedure.

5.1.3 Analytical control

After homogenising, the concentration of anionic and non-ionic surfactants in the detergent is determined according to the MBAS and BiAS analytical procedure. The soap content is determined by a suitable analytical method.

This analysis of the product is necessary to calculate the quantities required preparing fractions for the biodegradability tests.

Quantitative extraction is not necessary; however, at least 80 % of the non-ionic surfactants should be extracted. Usually, 90 % or more is obtained.

5.2. Principle

From a homogeneous sample (powders, dried paste and dried liquids) an ethanol extract is obtained which contains the surfactants, soap and other alcohol-soluble constituents of the detergent sample.

The ethanol extract is evaporated to dryness, dissolved in an isopropanol/water mixture and the solution obtained is passed through a strongly acidic cation exchange/macro-porous anion exchange combination heated to 50 °C. This temperature is necessary to prevent the precipitation of any fatty acids which may be present in acidic media. The non-ionic surfactants are obtained from the effluent by evaporation.

Cationic surfactants, which might upset the degradation test and the analytical procedure, are eliminated by the cation exchanger placed above the anion exchanger.

5.3. Chemicals and equipment

5.3.1. *Deionised water*

5.3.2. *Ethanol, C₂H₅OH 95 % (v/v) (permissible denaturant: methyl-ethyl ketone or methanol)*

5.3.3. *Isopropanol/water mixture (50/50 v/v):*

– 50 parts by volume isopropanol, CH₃CHOH.CH₃, and

– 50 parts by volume water (5.3.1)

5.3.4. *Ammonium bicarbonate solution (60/40 v/v):*

0,3 mol NH₄HCO₃ in 1 000 ml of an isopropanol/water mixture consisting of 60 parts by volume isopropanol and 40 parts by volume water (5.3.1)

5.3.5. *Cation exchanger (KAT), strongly acidic, resistant to alcohol (50-100 mesh)*

5.3.6. *Anion exchanger (AAT), macro-porous, Merck Lewatit MP 7080 (70-150 mesh) or equivalent*

5.3.7. *Hydrochloric acid, 10 % HCl w/w*

5.3.8. *2 000 ml round-bottomed flask with ground glass stopper and reflux condenser*

5.3.9. *90 mm diameter suction Filter (heatable) for filter papers*

5.3.10. *2 000 ml filter flask*

5.3.11. *Exchange columns with heating jacket and tap: inner tube 60 mm in diameter and 450 mm in height (see Figure 4)*

5.3.12. *Water-bath*

5.3.13. *Vacuum drying oven*

5.3.14. *Thermostat*

5.3.15. *Rotary evaporator*

5.4. Preparation of extract and separation of non-ionic active agents

5.4.1. *Preparation of extract*

The quantity of surfactant necessary for the degradation test is about 25 g BiAS.

In preparing extracts for the degradation tests, the quantity of product to be used should be limited to a maximum of 2 000 g. Therefore it may be necessary to carry out the operation two or more times in order to obtain sufficient quantity for the degradation tests. Experience has shown that there are advantages in using a number of small extractions rather than one large extraction.

5.4.2. *Isolation of alcohol-soluble constituents*

Add 250 g of the synthetic detergent to be analysed to 1 250 ml ethanol and heat the mixture to boiling point and reflux for one hour with stirring. Pass the hot alcoholic solution through a coarse-pored suction filter heated to 50 °C and filter rapidly. Wash the flask and suction filter with approximately 200 ml hot ethanol. Collect the filtrate and filter washings in a filter flask.

In the case of pastes or liquid products to be analysed, make sure that not more than 25 g anionic surfactants and 35 g soap are contained in the sample. Evaporate this weighed sample to dryness. Dissolve the residue in 500 ml ethanol and proceed as described above.

In the case of powders of low apparent density (< 300 g/l) it is recommended to increase the ethanol ratio in the relation 20:1.

Evaporate the ethanolic filtrate to complete dryness, preferably by means of rotary evaporator. Repeat the operation if a greater quantity of extract is required. Dissolve the residue in 5 000 ml isopropanol/water mixture.

5.4.3 *Preparation of ion-exchange columns*

CATION-EXCHANGE COLUMN

Place 600 ml cation-exchange resin (5.3.5) in a 3 000 ml beaker and cover by adding 2 000 ml hydrochloric acid (5.3.7). Allow to stand for at least two hours, with occasional stirring. Decant the acid and transfer the resin into the column (5.3.11) by means of deionised water. The column should contain a glass-wool plug. Wash the column with deionised water at a rate of 10-30 ml/min until the eluate is free of chloride. Displace the water with 2 000 ml isopropanol/water mixture (5.3.3) at a rate of 10-30 ml/min. The exchange column is now ready for operation.

ANION-EXCHANGE COLUMN

Place 600 ml anion-exchange resin (5.3.6) in a beaker and cover by adding 2 000 ml deionised water. Allow the resin to swell for at least two hours. Transfer the resin into the column by means of deionised water. The column should contain a glass-wool plug.

Wash the column with 0,3 M ammonium bicarbonate solution (5.3.4) until free of chloride. This requires about 5 000 ml solution. Wash again with 2 000 ml deionised water. Displace the water with 2 000 ml isopropanol/water mixture (5.3.3) at a rate of 10-30 ml/min. The exchange column is now in the OH form and ready for operation.

5.4.4. *Ion-exchange procedure*

Connect the exchange columns so that the cation-exchange column is placed on top of the anion-exchange column. Heat the exchange columns to 50 °C using thermostatic control. Heat 5 000 ml of the solution obtained in item 5.4.2 to 60 °C and pass the solution through the exchanger combination at a rate of 20 ml/min. Wash the columns with 1 000 ml hot isopropanol/water mixture (5.3.3).

To obtain the non-ionic surfactants collect the filtrate and filter washings and evaporate to dryness, preferably by means of a rotary evaporator. The residue contains the BiAS. Add deionised water until a defined volume is obtained and determine the BiAS content in an

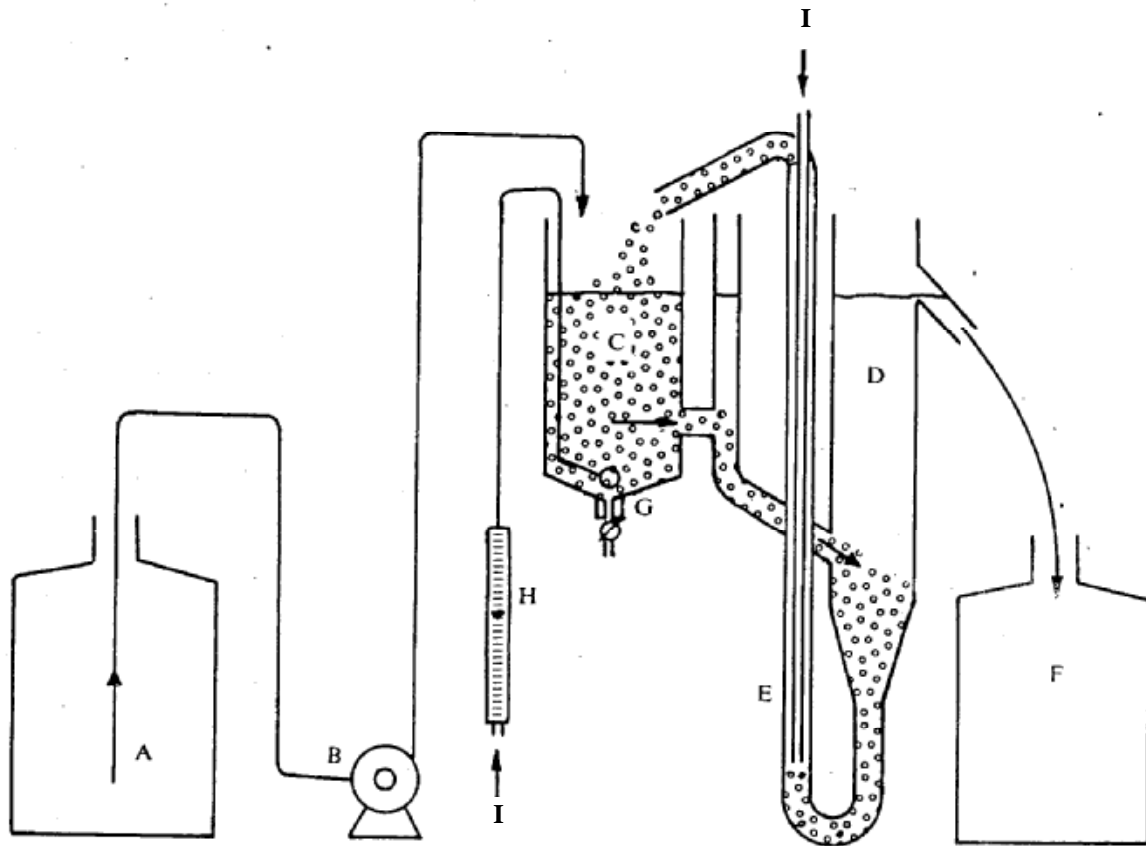
aliquot. The solution is used as a standard solution of non-ionic surfactants for the degradation test. The solution should be kept at a temperature below 5 °C.

5.4.5. Regeneration of ion exchange resins

The cation exchanger is rejected after use.

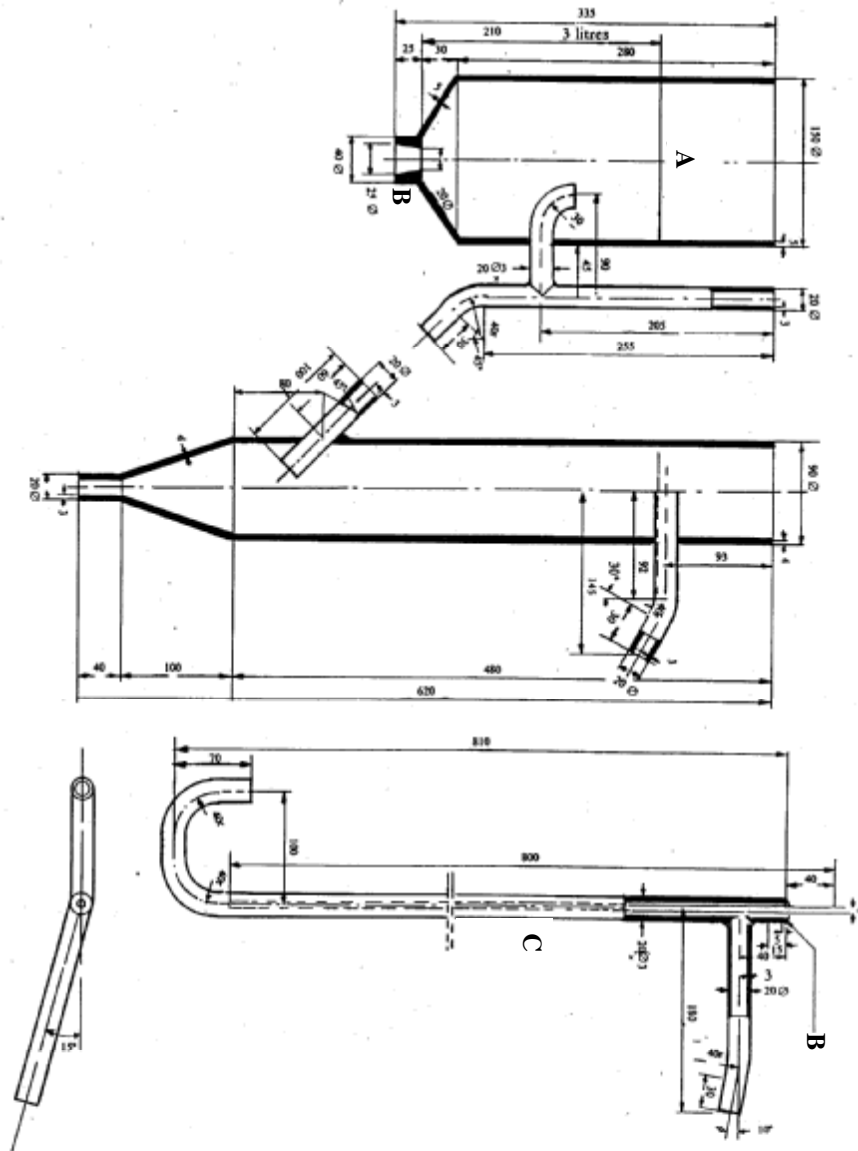
Passing about 5 000-6 000 ml of ammonium bicarbonate solution (5.3.4) down the column at a flow rate of approximately 10 ml/min until the eluate is free from anionic surfactants (methylene blue test) regenerates the anion-exchange resin. Then pass 2 000 ml isopropanol/water mixture (5.3.3) down the anion exchanger to wash. The anion exchanger is again ready for operation.

Figure 1
Activated sludge plant: overviews



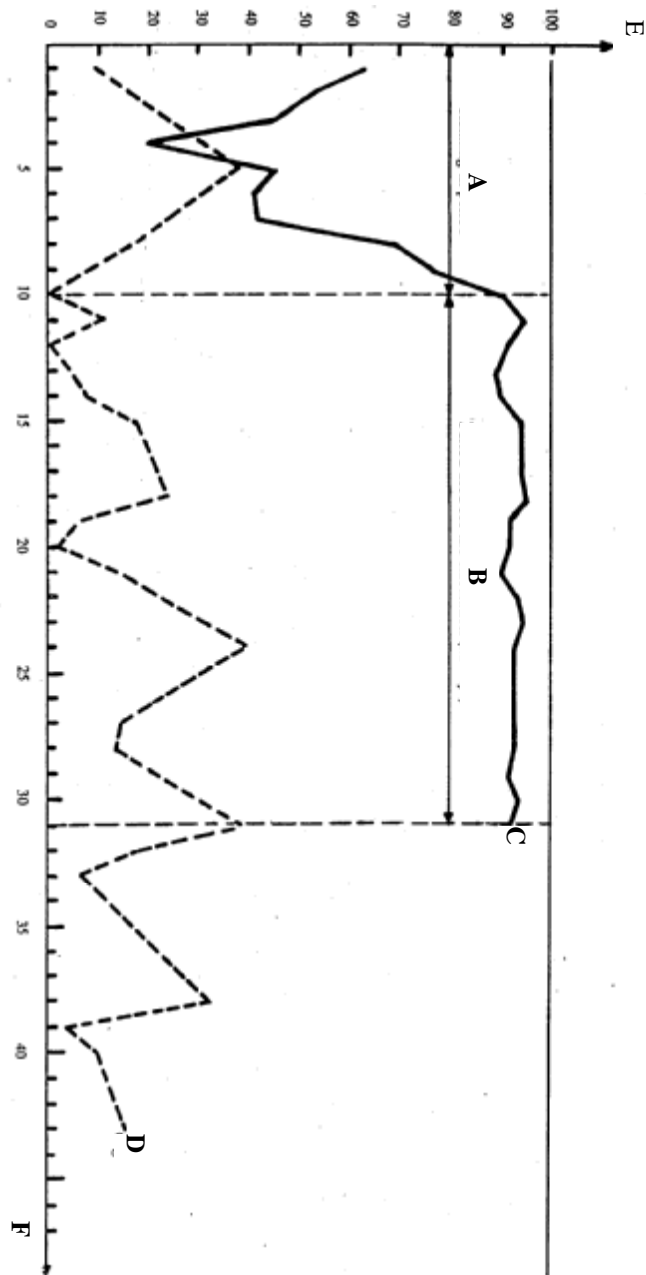
- A. Storage vessel
- B. Dosing device
- C. Aeration chamber (*three litres capacity*)
- D. Settling vessel
- E. Air-lift pump
- F. Collector
- G. Sintered aerator
- H. Air-flow meter
- I. Air

Figure 2
Activated sludge plant: detail
 (dimensions in millimetres)



- A. Liquid level
- B. Hard PVC
- C. Glass or waterproof plastic (hard PVC)

Figure 3
 Calculation of biodegradability – Confirmatory test



- A. Running-in period
- B. Period used for calculation (*twenty-one days*)
- C. Readily biodegradable surfactant
- D. Surfactant not readily biodegradable
- E. Biodegradation (%)
- F. Time (days)

Figure 4
Heated exchange column
(dimensions in millimetres)

