Determination of the Adsorption Characteristics of Organic Test Substances in Sewage Treatment Processes (Tentative Method) 1992

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About This Series

This booklet is part of a series intended to provide recommended methods for determining the quality of water and associated materials. In addition short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series is published as a series of booklets on single or related topics, thus allowing for the replacement or addition of methods as quickly as practicable without the need for waiting for the next edition. The rate of publication is also related to the urgency of the requirement for that particular method.

Although ideally, all methods published should be fully tested, this is not often possible without delay in publication. Furthermore, the limit of detection, range, precision and interference effects applying to instrumental methods can depend on the actual instrument used, as well as on sample type, reagent purity and operator skill, etc. Even methods tested in many laboratories have been known to acquire problems when new products appear (introducing new substances into effluents), changes in production methods affecting reagent quality, or the method used to analyse new types of sample (despite apparent similarity to samples already evaluated). As a guide, the following categories have been given to methods:

(i) tested, usually in five or more laboratories
- no grade indicated;

(ii) tested in one to three or four laboratories
- Tentative;

(iii) evaluated, but not fully tested, but publication is urgently required
- Note;

(iv) tested and found to be satisfactory by several laboratories, but in the opinion of experts requires a high degree of skill or has some other difficulty such that the method would be replaced if a better method were discovered.
- Provisional.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users and senior technical staff, to decide which method to use for the determination in hand. Whilst the attention of users is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has nine working groups each responsible for one section or aspect of water cycle quality analysis. They are:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage works control methods
9.0 Radiochemical methods.

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and the main committee. The names of those associated with this method are listed at the back of this book.

Publication of new or revised methods will be notified to the technical press. A current list of publications can be obtained from the Secretary.

Every effort is made to prevent errors from occurring in the published text. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically. However, should any errors be found, please notify the Secretary.

DR D WESTWOOD
Secretary

29 January 1992

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety and COSHH Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text, so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown to be often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', issued by the Royal Society of Chemistry, London: 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Services Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient, give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Safety while Sampling

Prior consideration must be given, especially when sampling in confined spaces or where access is difficult, to guard against suffocation, drowning, falls and poisoning or infection by ingestion, inhalation or skin contact.

Good Laboratory Practice

The Department of Health issues a booklet entitled: Good Laboratory Practice; the United Kingdom Compliance Programme, 1989. This can be obtained by writing to that Department in London. It deals chiefly with toxicity studies, but much can be applied to analytical chemistry.

Determination of the Adsorption Characteristics of Organic Test Substances in Sewage Treatment Processes (Tentative Method) 1992

Introduction

Certain chemicals, when discharged to sewer, may bind either chemically or physically to particulate matter present in sewage. The extent of binding depends on both the physico-chemical properties of the chemical (eg water solubility, ionic charge) and the nature of the sewage (eg suspended solids concentration, particle size distribution).

At a sewage treatment works, the next step after gross solid matter and grit removal, is to eliminate as much of the remaining suspended solids as possible, so as to reduce the strength of the sewage and render it more amenable to biological oxidation. Suspended solids removal is usually effected in either quiescent or continuous flow primary sedimentation tanks. The settled solids from this process may be digested under anaerobic conditions, incinerated or otherwise treated before land or sea disposal, and the supernatant is subjected to biological oxidation in either the activated sludge or the biological filter process.

In order to calculate the concentration of a chemical entering both aerobic and anaerobic sewage treatment, it is necessary to know how it partitions between primary sludge and the settled sewage produced as a result of primary sedimentation. This method describes a procedure for determining the partitioning of a chemical and the use of the data produced is discussed in the context of selecting appropriate biodegradation and toxicity tests and the amounts going to aerobic and anaerobic treatment.

1 Performance Characteristics of the Method

1.1	Parameter determined	The degree to which organic substances partition between sludge and supernatant in the primary sedimentation process, and between sludge and liquid phase in activated sludge mixed liquor.
1.2	Types of sample	Organic substances, soluble at the test concentrations, either pure or in commercial formulations, for which a specific method of analysis exists. When activated sludge is used, dissolved organic carbon analysis may be used as an alternative procedure.
1.3	Basis of method	A range of concentrations of the test substance are shaken in crude domestic sewage or activated sludge mixed liquor for a period of 1 hr at 20 ± 5°C: The solids are allowed to settle for 1 hr and the concentration of substance remaining in the supernatant liquor is determined after this time.
1.4	Range of application	0–100% adsorption onto sludge may be measured. The method as written is not applicable to volatile substances, but could be modified if necessary. Although this method is primarily intended for determining adsorption in sewage, it has potential for use in soil/sediment adsorption studies.
1.5	Standard deviation	Not known.

1.6	Limit of detection	Depends on the sensitivity of the analytical method used for determining the test substance.
1.7	Sources of error	Substances naturally present in the sewage may interfere with the analysis of the test substance. Crude sewage samples may vary considerably depending on source and time of sampling.
1.8	Time required for analysis	Total time required, 8 hr; operator time 4 hr for one substance (excluding analysis which depends on the method used).

2 Principle

The test substance, at a range of concentrations, is shaken in either crude sewage or activated sludge for 1 hr. The sewage solids are allowed to settle for 1 hr and then the concentration of the chemical remaining in the aqueous phase is determined by a specific analytical method, or if activated sludge is used as dissolved organic carbon.

3 Interferences

An analytical method specific for the test substance is essential when crude sewage is used and it must be shown that this is not subject to major interferences from compounds naturally present in the sewage. When activated sludge is used, it is possible to use dissolved organic carbon measurements.

4 Hazards

4.1 Hygiene

Since crude sewage and activated sludge are obtained from a sewage treatment works, suitable precautions should be taken to avoid infection from the potentially pathogenic micro-organisms present in the unknown mixed population.

4.2 Chemicals

If the test substance is toxic or its properties are unknown, it should be handled with care.

5 Reagents

5.1 Deionised or distilled water

5.2 Stock solution of the test substance. A stock solution of the test substance is prepared in distilled or deionised water to contain 1,000 $mgl.^{-1}$. If the test substance is not 100% pure or is a formulation, the concentration should be adjusted to give a solution containing 1,000 $mgl.^{-1}$ of the substance of interest.

5.3 Stock solution of the reference substance. A stock solution of the reference substance is prepared in distilled or deionised water to contain 1,000 $mgl.^{-1}$. It is advisable to check periodically the adsorption characteristics of the crude sewage used. A suitable reference substance is cetyl trimethyl ammonium bromide.

5.4 Crude sewage and activated sludge. These are obtained from a plant treating predominantly domestic sewage. Crude sewage should be freshly collected from the inlet to the primary sedimentation tanks. Activated sludge can be collected from either the aeration tank or the return sludge line.

6 Apparatus

6.1 1 litre measuring cylinders

6.2 Magnetic stirrers capable of maintaining solids in suspension.

6.3 Suitable analytical equipment to determine the concentration of the test substance in the range 0.1-20 $mgl.^{-1}$. A dissolved organic carbon analyser may also be used.

6.4 Centrifuge capable of operation at 4,000 rpm. Membrane filtration (0.45 μm) is an alternative procedure.

7 Test Procedure

7A Using crude sewage

Step	Procedure	Notes
7A.1	Take a sample of crude sewage and determine the suspended solids content (Note a).	(a) Use the paper filtration method in this series (Ref 1).
7A.2	Set up a series of measuring cylinders containing the test substance at a range of concentrations together with appropriate controls (Note b).	(b) A suggested experimental design is shown in Table 1. When first using the method and at regular intervals thereafter, it is advisable to include a reference substance (section 5.3).
7A.3	Place a magnetic follower in each measuring cylinder and stir at ambient temperature for 1 hr (Note c).	(c) The ambient temperature should be 20 ± 5°C. The stirring speed should ensure that all solids are kept in suspension.
7A.4	Remove the measuring cylinders from the stirring apparatus and remove the magnetic followers (Note d). Allow the solids to settle for 1 hr at ambient temp (Note e).	(d) If the objective of the experiment is to determine the Freudlich isotherm only, proceed to the centrifugation stage (step 7A.7). (e) At approx 20 min intervals gently dislodge, using a glass rod, any solids adhering to the sides of the cylinders. Take care not to disturb the settled solids.
7A.5	After 1 hr measure the settled sludge volume (V_1) and decant about 500 ml of supernatant taking care not to disturb the settled solids (Note f).	(f) The volume of supernatant which must be decanted depends on the analytical method.
7A.6	Thoroughly mix the supernatant and analyse for the test substance (Note g) as well as the suspended solids content (see Note a above).	(g) Analysis should be effected as soon as possible after sampling. If necessary a preservative can be added provided this does not interfere with the analytical method.
7A.7	Take a further aliquot of the supernatant from the sample prepared (7A.6) and centrifuge at 4,000 rpm for 10 min.	
7A.8	Decant the clear supernatant and analyse for the test substance (Note g).	

7B Using activated sludge

Step	Procedure	Notes
7B.1	Take a sample of activated sludge mixed liquor (5.4) and centrifuge at 4,000 rpm for 10 min (Note a).	(a) The quantity required depends on the concentration. A total of 3,000 mg mixed liquor suspended solids (MLSS) is required for the experiment shown in Table 1.
7B.2	Discard the supernatant and resuspend the solids in an equal volume of water.	

Step	Procedure	Notes
7B.3	Repeat the centrifugation in steps 7B.1 and 7B.2 twice, finally resuspend the sludge in a volume of test medium to result in a nominal concentration of 200 mgL^{-1} MLSS (Note b).	(b) Check this concentration by redetermining solids after washing.
7B.4	Follow procedure for crude sewage (7A), steps 7A.2-7A.8	

8 Calculation and Interpretation of Results

8.1 The percentage of the test substance remaining in the supernatant is calculated at each test substance concentration and an average value obtained for duplicates:

$$\%\ \text{remaining in supernatant} = \frac{(C_1 - C_B)(V - V_1)}{C_o V} \times 100$$

where C_o = Concentration (mgL^{-1}) of test substance added initially, corrected for recovery using the control containing no sewage.

C_1 = Concentration (mgL^{-1}) of test substance in supernatant from test cylinders.

C_B = Concentrations (mgL^{-1}) of test substance in supernatant from cylinders containing sewage only.

V = Total volume of cylinder contents (usually 1 litre).

V_1 = Volume (in litres) of settled solids at time t = 1 hr.

8.2 Check the dependence of % test substance remaining in supernatant on the initial concentration taken for test. If the % remaining in the supernatant is constant, this indicates that the test substance has not been preferrentially adsorbed onto the solids and the value obtained should be equal to $\frac{V - V_1}{V} \times 100$.

8.3 If the percentage test substance remaining in the supernatant decreases with decreasing test substance concentration this suggests that adsorption onto solids has occurred. Determination of the test substance concentration in centrifuged supernatants allows calculation of the degree of adsorption:

$$A = \frac{C_1 - C_2}{x} = \text{mg test substance/mg solids}$$

where C_2 = concentration (mgL^{-1}) of test substance in centrifuged supernatant.

x = suspended solids (mgL^{-1}) in supernatant.

A = concentration of test substance in solids ($mg\ mg^{-1}$).

8.4 Plot log (A) versus log C_2. If the relationship is linear then the Freudlich isotherm ($A = K.C_2^{1/n}$) may be applied in its logarithmic form ($\log A = \log K + 1/n \log C_2$) and the linear regression calculated, where n is a constant. If the regression is significant (for N = 5, P = 5%, $R^2 > 0.77$) then the adsorption constant K can be calculated from the intercept on the Y axis (= log K). For information on regression analysis and the meaning of N (number of results), P (probability) and R (regression constant) see Ref 2.

If the relationship is not linear an estimate of K can still be calculated from:

$$K = \frac{A}{C_2}$$

Where K can be determined at several values of C_2 where the latter is measurable (30-70% adsorption) and an average value obtained.

8.5 From the above data the partitioning of the test substance, between primary settled sewage (including fine solids in suspension) and primary solids (sludge), can be determined. If there is no preferential adsorption onto the solids it can be assumed that the concentration of test substance passing to both biological oxidation (activated

sludge/trickling filter) and anaerobic digestion (or other sludge disposal option) is equal to that in the inflowing crude sewage.

If significant adsorption is apparent then it may be necessary to conduct additional crude sewage settlement experiments to determine solids settlement efficiency and hence the concentration of test substance remaining in the primary settled sewage. In general, primary solids separation processes are 50–70% efficient and 30–50% of the solid matter remains in suspension as fine solids. Clearly, a significant proportion of even highly adsorbed substances will still pass to aerobic sewage treatment processes. In this case, both aerobic and anaerobic toxicity tests will be indicated. If biodegradation tests are to be conducted on highly adsorbed substances, care must be taken to differentiate between removal by adsorption and biodegradation.

9 Sources of Error

9.1 The method relies on the accuracy of the analytical procedure for the test substance. The method of analysis should be checked before use, to ensure good recovery of the test substance from crude sewage or activated sludge spiked with known quantities.

9.2 Crude sewage and activated sludge should be selected carefully for use in this experiment. Both should be obtained from a treatment works which does not receive a significant industrial effluent input.

9.3 The test does not distinguish between removal of the substance by adsorption and biodegradation. Significant biodegradation of the test substance is unlikely within the 2 hr test period, but if this is suspected it may be prudent to determine the concentration of test substance adsorbed on the sludge in order to obtain a mass balance.

9.4 Some of the above sources of error (9.1 and 9.2) can be minimised by use of ^{14}C labelled test substances.

10 References

1. Methods for the Examination of Water and Associated Materials *Suspended, settleable, and total dissolved solids in waters and effluents*, 1980, in this series, HMSO, London. ISBN 0 11 751957 X

2. Snedecor G W and Cochran W G, *Statistical Methods* Iowa State University Press 1988 ISBN 813815606

Table 1 Suggested Experimental Design for Determination of the Partitioning of a Test Substance in Crude Sewage or Activated Sludge

Cylinder No	Test substance		Crude sewage or activated sludge* (mL)	Water (mL)	Total volume (mL)
	Concentration (mgL^{-1})	Vol of $1gL^{-1}$ stock (mL)			
1, 2	20	20	980	—	1,000
3, 4	10	10	980	10	1,000
5, 6	5	5	980	15	1,000
7, 8	2	2	980	19	1,000
9,10	1	1	980	19	1,000
11,12	0	0	980	20	1,000
13,14	20	20	0	980	1,000

*The activated sludge concentration is 200 mgL^{-1}
See section 7A.2

Address for correspondence

However well a method is tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:

The Secretary
The Standing Committee of Analysts
Department of the Environment (Drinking Water Inspectorate)
Romney House
43 Marsham Street
LONDON
SW1P 3PY

Standing Committee of Analysts

Members assisting with this method

H T Barnhoorn	2	R Law	2
F B Basketter	2	J J Monaghan	2
N S Battersby	1	C J Nash	1
D J Bealing	1	P N R Nichols	2
G A Best	2	H A Painter	1, 2
R R Birch	1	L R Pittwell	2
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P Hiley	1	R H West	2
M R Hurcombe	2	O A Williams	2
J Jeffrey	2	K Wheatstone	2
J G Jones	2	R Wood	2

1 Working group member
2 Main committee member

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