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Methods for

Sampling chemical products —

Part 1: Introduction and general
principles

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- British Colour Makers' Association
- British Tar Industry Association
- Chemical Industries Association
- Department of Industry, Laboratory of the Government Chemist
- Fertiliser Manufacturers' Association
- Institute of Petroleum
- Institute of Trading Standards Administration
- Institution of Gas Engineers
- Ministry of Defence
- Society for Analytical Chemistry
- Standardization of Tar Products Tests Committee
- United Kingdom Atomic Energy Authority

The following were directly represented on the committee entrusted with the preparation of this Part of this British Standard:

- Chairmen of subcommittees of BSI Technical Committee C/38
- Institute of Petroleum

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Foreword

This British Standard has been prepared under the authority of the Chemical Divisional Council following a conference convened by the British Standards Institution at which agreement was reached on the importance of standardizing techniques and apparatus for obtaining representative samples of chemical products.

The other Parts of this British Standard are as follows:

- *Part 2: Sampling of gases;*
- *Part 3: Sampling of liquids;*
- *Part 4: Sampling of solids;*
- *Part 5: Probability theory applied to sampling (under consideration).*

The Parts of this British Standard are intended to provide a basis for specifying methods of sampling in other British Standards, and also to act as a guide to manufacturers and users of materials not covered by British Standards.

Therefore this standard is not intended to be used as working instructions for the person who actually takes the sample. It is essential that users of the other Parts shall first read Part 1 so that they will be competent to develop a detailed procedure for sampling any quantity of a given product.

International Standards, partly based on the contents of this British Standard, are in course of preparation by Technical Committee 47 (Chemistry) of the International Organization for Standardization (ISO). In particular, the contents of section six are technically identical with those of Draft International Standard ISO/DIS 3165 “Sampling of chemical products for industrial use — Safety in sampling”.

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

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

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 30, an inside back cover and a back cover.

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

Section 1. General

1 Scope

This British Standard specifies methods for the sampling of chemical products in gaseous, liquid or solid form. This Part of the standard discusses the principles of sampling and is intended to assist users of Parts 2 to 4 in developing a detailed procedure for sampling any quantity of a chemical product.

2 References

The titles of the British Standards referred to in this standard are listed on the inside back cover.

3 Definitions

For the purpose of this British Standard the following definitions apply.

3.1 General terms

3.1.1 item

a defined quantity of material having a boundary which may be either physical, e.g. a container, or hypothetical, e.g. at a particular time and interval in a stream

NOTE 1 A number of items may be gathered together, e.g. in a package or box.

NOTE 2 The terms individual and unit are sometimes used as synonyms of item.

3.1.2 sample

one or more portions of material derived from a larger amount in one item, or one or more items taken from a larger number of items

NOTE 1 A sample may be one portion or unit or the collection of the portions or units.

NOTE 2 The word specimen is used in certain cases as an alternative to sample, especially in connection with the sampling of discrete materials

3.1.3 representative sample

a sample assumed to have the same composition as the material sampled when this is considered as a homogeneous whole

3.1.4 sampling plan

the planned procedure of allocation, withdrawal and preparation of a sample or samples from a lot (see 3.2.1) to yield the required knowledge of the characteristic(s) (see 3.2.16) from the final lot sample (see 3.2.9) with a minimum cost, effort or delay appropriate to an acceptable sampling error so that a decision can be made regarding the lot

3.1.5 consignment

a quantity of material covered by a particular consignment note or shipping document

3.2 Hierarchy of sampling terms

3.2.1 lot

the total material to be sampled using a particular sampling plan. It may consist of a number of consignments, batches or items

3.2.2 batch

a definite quantity of material that may be one item or a number of items which belong together because of their manufacture or production under conditions which are presumed to be uniform

3.2.3 sub-item

the practical or hypothetical division of an item in connection with the assessment of variability

3.2.4 primary sample

one or more samples taken from the one or more items constituting the lot, or a number of items selected from the total items constituting the lot. When collected together it is essential for the individual samples of a primary sample to maintain their identity

3.2.5 bulk sample

a collected set of samples which do not maintain their individual identities

3.2.6 blended bulk sample

a collected set of samples blended together to obtain a uniform sample

3.2.7 composite sample

a blended bulk sample, the individual samples of which have been taken in amounts proportional to the quantity of the material that they represent

3.2.8 reduced sample

a sample that has been obtained by reducing the quantity of another sample without change of composition

NOTE It may be necessary to reduce the particle size also in the course of reducing the quantity.

3.2.9**final lot sample**

the final sample obtained or prepared under the sampling plan for possible subdivision for testing, reference or storage

3.2.10**laboratory sample**

a sample, intended for inspection or testing, prepared from the final lot sample or otherwise obtained

3.2.11**reference sample**

a sample, prepared from the final lot sample at the same time as and identical with the laboratory sample, accepted by the parties to a contract and which is held for use as a laboratory sample in the case of a dispute

3.2.12**storage sample**

a sample, prepared from the final lot sample at the same time and identical with the laboratory sample, intended for possible future use as a laboratory sample

3.2.13**test sample**

the sample prepared from the laboratory sample from which the test portions are withdrawn or taken

3.2.14**test portion**

the portion withdrawn or taken from the test sample and used in the test or observation

3.2.15**test or observation**

an operation made in order to measure or classify a characteristic

3.2.16**characteristic**

a definable property of the material. It will differentiate either qualitatively (by attributes) or quantitatively (by variables)

3.3 Terms related to taking a sample**3.3.1****spot sample**

a sample of specified number or size taken from a specified place in the material or at a specified place and time in a stream and representative of its own local environment

3.3.2**geometric sample**

a sample of specific geometric shape whose dimensions are related to the axes of variability of material in an item

3.3.3**cross-sectional sample**

a geometric sample large in only two dimensions each of which is related to one of the two principal axes of variability of material in an item

3.3.4**directional sample**

a geometric sample large in only one dimension which is related to the single principal axis of variability of material in an item

3.3.5**surface sample**

a sample taken at the surface of the material and intended to yield information about the material at that surface

3.3.6**bottom sample**

a sample taken at the lowest point of the material and intended to yield information about the material at that point

3.3.7**upper sample**

a spot sample taken in a liquid at a level of one-sixth of the volume of the liquid, below its surface

3.3.8**middle sample**

a spot sample taken in a liquid at a level of one-half of the volume of the liquid, below its surface

3.3.9**lower sample**

a spot sample taken in a liquid at a level of five-sixths of the volume of the liquid, below its surface

3.3.10**continuous sample**

a sample taken continuously from a stream so as to obtain a representative sample

3.3.11**intermittent sample**

a sample taken intermittently from a stream so as to obtain a representative sample

3.3.12**automatic sampler**

a device which, when correctly installed and when activated by appropriate control equipment, enables a representative sample of flowing material to be taken automatically

3.3.13**self-actuated sampler**

an automatic sampler that is operated by material flow or pressure

3.3.14**externally actuated sampler**

an automatic sampler that is operated by a power source other than the material being sampled, e.g. an electric or pneumatic motor

3.3.15**reduction**

- a) The process which reduces the quantity of the sample.
- b) The process which reduces the particle size of the material constituting the sample.

3.3.16**ullage (outage)**

the capacity of a container not occupied by the material, or the distance between the surface of the material and some fixed reference point at the top of the container

NOTE In the case of a liquid this allows for its expansion.

3.4 Terms relating to the statistics of sampling**3.4.1****true value**

the unequivocal value of a characteristic of the material. The true value is an ideal notion and in general it cannot be known

3.4.2**average lot quality**

the result that would theoretically be obtained by taking the average of results from a large number of laboratories of replicate determinations of a characteristic, by the test method in question, made on replicate representative samples taken from the lot (see 10.1)

3.4.3**variability**

the differences throughout the material in the value of a characteristic

3.4.4**homogeneous material**

material in which the mean values of the characteristic(s) under consideration of the component portions are not significantly different (see 13.2)

3.4.5**heterogeneous material**

material in which the mean values of the characteristic(s) under consideration of the component portions show significant variation (see 13.3)

3.4.6**defect**

a failure of an item to meet a specified requirement for the value of a characteristic

3.4.7**defective item**

an item containing one or more defects

3.4.8**error**

a discrepancy from what is true or right (see clause 12)

3.4.9**accuracy**

the closeness of test results to the true value (see 3.4.1)

3.4.10**precision**

the closeness of agreement between the results obtained for the same characteristic of identical test material, by applying the test procedure several times

3.4.11**sampling error**

the error arising from known and acceptable deficiencies in the sampling plan

Section 2. Purposes of sampling**4 Introduction**

The purposes of the sampling operation should be clear so that an appropriate sampling plan is devised. In addition to the fundamental purpose, it is necessary to consider the commercial purposes for which the sampling is required before a plan is developed (see clauses 6 and 7).

5 Fundamental purpose

Samples are taken from larger quantities or numbers in order that on examining the samples certain information pertaining to the whole may be obtained. Such a procedure is necessary when the testing of the whole is impracticable. The process of sampling requires a sampling plan that will be satisfactory if it yields the information sought, allowing for known sources of error, at an acceptable cost. Two sources of error affect the information obtained:

- a) the failure of the sample or samples to represent the whole;
- b) inaccuracies in the test result
 - 1) resulting from failure to apply the appropriate techniques to determine the chosen characteristics of the sample,
 - 2) inherent in the test method used which may be ascertained from the precision quoted for the method.

6 Commercial purposes

The fundamental purpose is relevant to all types of sampling but the commercial purposes of sampling can be conveniently divided into four groups: economic, technical, legal and safety purposes. Although safety can be said to be a technical purpose, its importance is stressed by putting it in a separate section.

6.1 Economic purposes

- a) To serve as a basis for offer for sale.
- b) To ensure that a material purchased complies with a contract specification.
- c) To ensure that material for sale to customers satisfies the manufacturer's sales specification.

6.2 Technical purposes

- a) To facilitate quality control, process control, or inspection during the process of production or manufacture.
- b) To determine the nature, quantity and/or source of contaminants.
- c) To establish the identity of unknown materials.
- d) To confirm the identity of supposedly known materials.
- e) To ensure that a given material is suitable for the purpose for which it is intended to be used.
- f) To determine whether a recovered material is suitable for reuse in a process.
- g) To determine the changes in the characteristics of a material with time.
- h) To determine the source of a given material.

6.3 Legal purposes

- a) To ensure that material satisfies statutory requirements.
- b) To ensure that effluents from a processing site conform to permitted composition limits.
- c) To provide material for forensic investigations.
- d) To assess material for statutory liability.
- e) To assess material for arbitration purposes.

6.4 Safety purposes

- a) To establish whether a given physical situation is safe or hazardous.
- b) To help establish the cause of an accident.
- c) To classify the hazards of the material.

7 Information to be determined

Examination of the laboratory samples will provide information about two specific properties of the whole material.

- a) The average value of a characteristic of it. A special case of this is where it is required to state whether or not the average value of the characteristic complies with a specification.
- b) The variability of a characteristic throughout it. A special case of this is where it is required to state what proportion of items is defective.

Section 3. Sampling plan

8 Introduction

It is essential to plan sampling so that the required information, allowing for known sources of error, is obtained at an acceptable cost.

9 Factors affecting the sampling plan

9.1 Summary. The following factors affect the sampling plan once the decision as to the purpose of the sampling has been decided as in section two.

- a) The boundaries (see **9.2**), physical state and nature of the whole quantity to be examined.
- b) The likelihood of contamination or other deterioration in quality of the whole quantity during or since production or manufacture.
- c) The acceptable sampling error (see **9.3**).
- d) The specification to which the material is being examined (see **9.4**).
- e) The definition of the characteristics which are to be used as criteria for the decisions to be made about the material.
- f) The precision limits of the test methods used to ascertain the required characteristics.

g) The total and unit intrinsic value of the material.

h) The economics of the operation, and the physical and human resources available.

9.2 Definition of the boundaries. The unambiguous statement of precisely what material is to be examined requires that boundaries are defined that include all the material to be sampled and exclude all other material. Frequently the appropriate boundaries are obvious, for example both vendor and purchaser will usually consider a single consignment as a lot and will require a sampling plan aimed at reporting on such a lot. Similarly the output from a batch process will frequently be segregated in batches which are examined individually.

Continuous production does not offer such natural boundaries and when materials are flowing in continuous streams it is necessary to establish arbitrarily chosen time boundaries in order to define the quantity to be examined. For example, one might choose to regard the material moving past a particular point during a specified interval as a single entity, equivalent to a batch.

9.3 Sampling error. In all cases, a statement of acceptable error is necessary in order to design the sampling plan. All sampling plans, however conceived, contain an implied acceptance of error in the final estimate. It is desirable that the economic or other risks involved in accepting an unsatisfactory, or rejecting a satisfactory, quantity of material should be assessed and monitored.

9.4 Specifications and the sampling plan

9.4.1 If the ultimate objective of sampling and analysis is to establish whether or not the quality of the material being examined complies with a specification, e.g. a British Standard, then the specification may influence decisions on sampling. To some extent, therefore, the sampling plan begins with the specification.

9.4.2 The ideal specification will define unambiguously those characteristics necessary and sufficient to ensure fitness for the purpose for which the goods are supplied. General specifications, such as those included in British Standards, which are of general application may often include characteristics which are irrelevant to a special purpose but, on the other hand, may need to be supplemented by additional requirements for such purposes. Some existing standards note the more commonly required additional requirements.

For example, BS 3674 states that if, in addition to the chemical analysis, the purchaser and vendor agree to specify the pouring density, the quantity of sample required will be 2 kg rather than 500 g. For some users of soda ash, however, the sieve analysis of the material is also important and if this is specified it will usually affect the manner of sampling because particle size distributions are peculiarly susceptible to sampling bias.

9.4.3 It is necessary to consider the precise meaning of the limits or boundary values given to requirements. If, for example, a standard requires that the sodium oxide content of a substance determined in a specified manner shall be not less than 58.0 %, then assuming that a 20 tonne lot in 100 kg hessian bags, when sampled and tested, gives a result of 58.1 % and it is known that the 95 % confidence limits for the result are ± 0.2 %, there is obviously a chance that another sampling and analysis would give a result of less than 58.0 %. Equally, if the first result were 57.9 % (i.e. below the specified limit), repeated sampling and analysis could eventually give a result of 58.0 % or more; indeed it is possible that most of the repeated results would lie on the upper side of the specified limit.

The ambiguity cannot be completely removed by refining the techniques of sampling and testing; if there is a need to specify a limit, it is implied that there is some possibility of defective material being made or supplied and the result of sampling and analysis is always an estimate that is subject to some error, however small.

The best solution to this dilemma is to set the requirement at a value which is acceptable to both parties and if necessary to specify additionally the acceptable confidence limits for the sampling and testing. Thus in the example given, assuming the agreed requirement is 58.0 % and both parties can achieve 95 % confidence limits of ± 0.2 %, the vendor will deliver without reservation all material tested at 58.0 % or over. He is then accepting some risks of rejecting (i.e. not despatching) material which in fact is satisfactory. The purchaser on the other hand is also accepting the risk of material with a true Na_2O content of say 57.8 % being sent to him.

It is therefore recommended that in all cases, unless there is some special agreement to the contrary, a specification requirement should be interpreted as representing the desirable value of that characteristic which is the subject of the specification, rather than an absolute limit. The result obtained from analysis of a consignment should be accepted as the best available estimate of the mean value of the characteristic for the lot and neither party to a transaction should add to or subtract from this result any further margin or confidence limit.

9.4.4 It is desirable that a specification agreed between a supplier and a customer should be such that it does not impose an unwarranted burden on the supplier and is not so close to a critical value that difficulties may be imposed on the customer. Both parties should understand the risks involved in any sampling and testing procedure; failure to do so may lead to unprofitable recriminations and arguments about differences in results which have arisen by chance.

9.4.5 If suitable specifications do not exist, the sampling and testing may be undertaken for the purpose of establishing such specifications. The costs of sampling and testing should be considered in relation to the value of the materials when establishing or amending a specification, so that the specification is not made unnecessarily restrictive.

9.4.6 Specification limits should be fixed so as to make allowance for random errors inherent in the sampling and testing procedures called for by the specification.

Section 4. Basic principles of sampling

10 Introduction

10.1 The average lot quality as defined in 3.4.2 is a theoretical test result of the mean value of the lot. The estimate of this mean value, if it could be carried out, would give a result which would include the errors due to sampling and testing. The mean value is therefore concerned with the results of sampling and testing a material, not with an intrinsic absolute which may or may not be measurable; the methods of sampling and testing are thus part of the specification of the characteristic being measured.

10.2 The practice of sampling stems from the theoretical possibility of dividing the lot into a number of smaller portions which may be separately examined. In general, precisely identical results would not be expected on each of the portions; the results would be scattered about the average lot quality of the whole. The range of such a collection of results on every portion from the lot may be expected to embrace the mean value of a characteristic of the lot, and also permits an estimate to be made of the variation of the measured characteristic throughout the lot. The observable pattern of variability is dependent on the size of the portion examined. Thus if the whole be divided into ten equal portions the mean values of the portions may be expected to cover a narrower range than will the mean values of the subportions obtained by further division of each portion again into ten equal parts. Any measure of variability should therefore include a statement of the size of the portions chosen.

10.3 If, instead of examining every portion, a selection of portions is examined, then the choosing and removal of the portions is a sampling operation. Further, if the selection is truly random then it can be shown that the average value of a characteristic measured in the selected portions is a sound and unbiased estimate of the average lot quality of the whole; if the portions selected are sufficient in number, the variability of the whole can also be estimated, and the accuracy of both these estimates may be stated in quantitative terms.

10.4 An economy of effort may be achieved by mixing together the selection of portions and taking a sample from this mixture for examination. However, in comparison with the examination of individual portions followed by averaging the results, the mixing of the portions followed by an individual examination gives a result subject to additional errors. These arise from the imperfection of all practical mixing systems and are subject to a larger random error in the results of the examination. A systematic error may also be introduced if the characteristic under examination does not blend linearly on the basis of mass or volume used for equalizing the portions.

This method for estimating the average lot quality of a characteristic does not enable an estimate to be made of the variability of the characteristic through the whole and therefore the reliability of the estimated average lot quality cannot be stated.

Some compensation for these errors can be achieved by replication of the whole operation, but the variability is not measurable on a portion to portion basis but only between the collections of portions.

In general, measurement of variability requires the separate examination of a number of parts of the lot, but where the degree of variability is known or assumed from past experience, measurement of the mean value of a characteristic may require only the examination of a single sample drawn from a mixture of a number of parts of the lot.

10.5 The whole practice of sampling materials is founded on the basic concepts outlined so far in this section. A detailed examination and discussion follows so that sampling plans can be properly designed and the errors estimated. It is considered that in any organization which applies substantial effort to sampling, there may be considerable opportunities for improving the efficiency of sampling and for effecting economies which can only be discovered by a more intensive study of the subject and the relevant statistics.

11 Measurement of variability

11.1 When one of the properties to be estimated is the variability of a characteristic, it is necessary to attach a precise meaning to the concept of variability and to specify the sub-items between which variability is to be measured. If the whole quantity under examination is presented to the sampler in discrete items, these will frequently be used as the items between which variability is measured. For example, the variability within a 10 tonne consignment packed in drums containing 50 kg each of the material will usually be most conveniently measured as the variability between individual drums. Considerations other than convenience may be more important. If the material is used in, for instance, 3 kg scoopfuls in a purchaser's processes, then variability between 3 kg sub-items may be a more useful measure of variability from the purchaser's point of view.

11.2 In the case of continuous streams of products and large quantities of solids in bulk etc., the choice of sub-items between which variability may be measured is made under different restrictions.

Dealing first with moving streams, the variability within the quantity of product passing a given point in 24 h may be specified, for example, in sub-items comprising all the material passing the reference point in periods of 1 h. Alternatively, equal quantities taken instantaneously at random times from the stream may be examined to assess variability between quantities of the size taken.

The choice of sub-items in a large bulk of material may take similar forms. In a stockpile of several hundred tonnes, the variability might be required between masses of about 1 tonne each or between much smaller quantities spaced through the bulk at chosen intervals. In both cases the physical selection of the sample is not likely to be easy and the use to which knowledge of the variability is to be put should be carefully considered; the choice of sub-item size should be based on the application of the data. If, for example, the stockpile is fed or discharged in 10 tonne lots it is more likely that knowledge of the variability between 10 tonne sub-items will be of value than between 1 tonne sub-items. If so, then examination of the incoming or out-going material in the items formed by the deliveries or consignments of 10 tonnes will be both more convenient and more meaningful than any other system.

12 Random and systematic errors

12.1 The estimate of a characteristic of a material under examination differs from the average lot quality by the error of the estimate. This deviation may arise from many causes, but in general the contributions to the total error from these causes may be classified as either random errors, or systematic errors (bias).

A random error is one which arises solely by chance; its specific characteristic is that the mean value of random errors tends to zero as the number of estimates made is increased by replication. All other errors are systematic.

For example, if it is desired to sample a box filled with a mixture of black and white balls in order to estimate the proportions of black and white, one method would be to choose two balls at random and record the result. Clearly the estimate obtained from one such sample is unlikely to be adequate because only three results are possible: both black, both white or one white and one black. It might therefore be decided to return the sample to the box and after thoroughly mixing, to take another sample of two balls, record the result, return the sample and continue in this fashion. The mean value of the estimates so obtained would then provide an ever closer estimate of the average lot quality of the relative proportions present in the box. In other words, the random error would tend to zero. In this example the random error is introduced by the choice of a sample quantity that is too small for its purpose; optimum sample size is discussed in clause 15.